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Environmental Research Center, Cincinnati, Ohio

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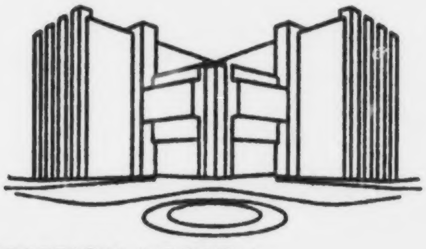
FEBRUARY 10-12, 1976



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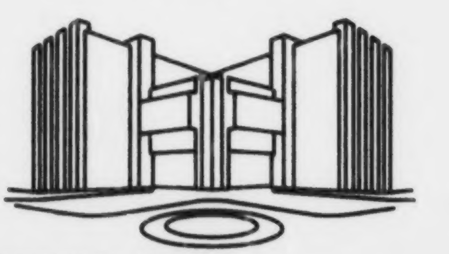

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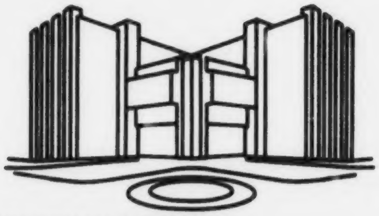

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FOREWORD

Municipal and industrial demands on water resources in the Polish Peoples Republic and the United States place increasing emphasis on the need for water pollution and abatement control research. These demands are recognized as important national concerns in both countries, and increased research efforts are being placed on wastewater treatment, sludge utilization, and renovated water use. Since 1972, the U.S. Environmental Protection Agency has conducted an extensive research program with the Polish Ministry of Administration, Local Economy and Environmental Protection and with the Ministry of Agriculture. The Symposium reported here highlighted the importance of cooperative international projects which are a part of each nation's research objectives; it serves to focus worldwide attention on a persistent and difficult environmental concern.

A forum for technical exchange among the Polish and American scientists and engineers engaged in cooperative projects was provided by the joint Symposium on Wastewater Treatment and Sludge Disposal held in Cincinnati, Ohio, February 10-12, 1976. In addition to the EPA and Polish representatives at the Symposium, academic and industrial scientists participated from the University of Cincinnati, Carnegie-Mellon University, Clemson University, and the American Iron and Steel Institute. Discussions focused on seven water-related projects, valued at approximately $1.4 million, that are being conducted in Poland under the Special Foreign Currency Program. These projects include studies of industrial wastewater from steel, textile, and tannery industries; biological and physical/chemical wastewater treatment technology; sludge utilization; and wastewater reuse.

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AGENDA OF SYMPOSIUM

Tuesday, February 10 — A.M.

Moderator: Francis M. Middleton

9:00 A.M.	Welcome to Cincinnati	Francis M. Middleton
	Opening Remarks	Dr. Thomas Murphy Thomas J. Lepine Stanislaw Nawara
9:30 A.M.	The Research Works on Sewage Treatment in Poland	Stanislaw Nawara
10:00 A.M.	Trends in Sludge Treatment and Disposal Practices in the United States	Dr. Joseph B. Farrell
10:30 A.M.	Break	
10:45 A.M.	Composting of Sewage Sludge and Solid Waste Matter	Dr. Jozef Cebula
11:15 A.M.	Effects of Water Works Sludge on Wastewater Treatment	Dr. Janusz Zakrzewski
11:45 A.M.	Discussion	
12:00 Noon	Lunch	

Tuesday, February 10 — P.M.

Moderator: John J. Convery

1:30 P.M.	Physical-Chemical Treatment of Combined Steel/Municipal Wastewater	Dr. Jan Suschka
2:00 P.M.	Comparison of Alternative Strategies for Coke Plant Wastewater Disposal	Dr. Robert W. Dunlap Dr. Francis C. McMichael
2:30 P.M.	Break	
2:45 P.M.	Tannery Waste Management	Dr. J. David Eye
3:15 P.M.	Discussion of Afternoon Papers *Discussion Leader:*	Dr. Herbert S. Skovronek

Wednesday, February 11 — A.M.

Moderator: Dr. Eugene E. Berkau

9:00 A.M.	Developing Treatment for Textile Wastes	Dr. Jan Suschka
9:30 A.M.	Textile Wastewater Treatment Methods Suitable for Recovery	Dr. John J. Porter
10:00 A.M.	Break	
10:15 A.M.	Removal of Refractory Substances from Textile Wastewater	Dr. Jerzy Kurbiel
10:45 A.M.	The EPA Research and Development Studies on Textile Wastewater	Thomas N. Sargent
11:15 A.M.	Discussion of Morning Papers *Discussion Leader:*	Thomas N. Sargent
11:45 A.M.	Lunch	

Wednesday, February 11 — P.M.

Moderator: Ms. Margaret J. Stasikowski

1:00 P.M.	Testing of Biodegradability and Toxicity of Organic Compounds in Industrial Waste Waters	Dr. Jan R. Dojlido
1:30 P.M.	Concept, Criteria and Measurements of Biodegradability	Dr. Robert L. Bunch
2:00 P.M.	Break	
2:15 P.M.	Renovated Water from Municipal Sewage Treatment Plants	Dr. Apolinary L. Kowal
2:45 P.M.	Wastewater Reuse Practice in the United States	Dr. Carl A. Brunner
3:15 P.M.	Discussion of Afternoon Papers *Discussion Leader:*	John N. English

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SUMMARY AND RECOMMENDATIONS

Environmental protection and enhancement are necessary and desirable goals for all nations. This Symposium on "Wastewater Treatment and Sludge Disposal" was a part of a much wider effort aimed toward environmental control. Wastewater treatment, both domestic and industrial, and the disposal of sludges are significant technical and economic problems in Poland and the United States.

The Symposium had significant impact on the joint Polish/U.S. projects. The open discussion of the papers, the injection of new ideas, and the demonstration of workable solutions to some problems will go far to ensure continued successful projects. Directions for future research were gained from the Symposium. The workshop attitude that prevailed among the 25 participants permitted intimate and fruitful discussion of the technical matter on both sides. The participants maintained an awareness that implementation of research results and attention to the problems of compliance are vital to ultimate environmental improvement.

The problems in both countries are similar. Water conservation and reuse, conservation of energy in environmental matters, combining sludge disposal techniques to gain some useful product or for economy of disposal, careful attention to land use for receiving wastewaters or sludges, disinfection techniques, the cross media effects of treatment and disposal technology are some of the areas of importance. Specific presentations in the Symposium dealt with wastes from municipalities, textile industries, iron and steel plants, water plants, and tanneries. Research results and needs on biodegradability were stressed. It was concluded that work in the two countries should complement each other. Close interchanges of information and experts between the countries aids this concept.

Some future topics for research were listed:

—Utilization of residue chars and other byproducts from the conversion and processing of coal

—Study of effects of using effluents on sludges (especially from older systems) on crops, soil, and groundwater quality

—Tertiary treatment of industrial wastewaters, including pulp and paper

—Disinfection of effluents and renovated waters.

Consideration was given to holding a symposium in Poland relating to mutual environmental interests of both countries. The topic is yet to be determined.

Proceedings of this Symposium have been printed in both Polish and English.

THE RESEARCH WORKS ON SEWAGE TREATMENT IN POLAND

Stanislaw Nawara

ABSTRACT

The rapidly accelerating social and economic development in Poland requires adequate institutional arrangements and scientific programs to deal with environmental protection. To solve the many environmental problems, the Polish Parliament has organized a governmental unit in the form of Ministry of Administration, Local Economy, and Environmental Protection.

Activities now encompass protection of the air, water, and soil as well as noise prevention. Water protection has been organized since 1954. The voivodship offices across the country have an important role in water pollution control. Adequate laws, regulations, and enforcement have been enacted to protect the waters of Poland.

About 80% of the water pollution in Poland comes from 2,800 industries and 600 towns. The largest contributors are the chemical, mining, power, food, and wood industries. Presently, about 60% of all wastewaters are treated.

Research for water protection is coordinated by the Environment Development Institute (EDI) and specialized institutes in individual ministries conduct the research projects. The EDI determines the standards, water quality norms, water classification, and anti-pollution programs. A plan has been made through 1985.

Present water quality improvement programs include 1. producing water and wastewater treatment equipment, 2. optimizing water reuse in industry, 3. encouraging the production of biodegradable detergents, pesticides, and other similar materials that are biodegradable, and 4. improving treatment methods, instrumentation, and information. Particular attention is being given to treating wastewater from small towns and tourist facilities. Advanced treatment processes are also under study to achieve the high quality water needed in some areas.

Protection of the Baltic Sea was agreed to in the 1974 Helsinki Convention. Poland is taking steps to meet the requirements for keeping the Baltic Sea clean.

INTRODUCTION

In the period of accelerated social and economic development of our country, the problems of environment protection have been accepted as a particularly important domain which presses for organizing adequate institutions, elaborating suitable forms of activity, and shaping a proper social attitude to these problems.

To solve these problems, the Polish Parliament created a competent organ of State Administration in the form of the Ministry of Administration, Local Economy, and Environment Protection. This Ministry includes activities concerning such problems as:

- waters and atmospheric air protection against pollutants,
- waste treatment,
- noise and vibration prevention,
- protection and recultivation of soils.

As the need arises and in view of their intensity, these activities can be expanded to include other environmental problems.

Among these environmental problems, protecting surface waters against pollution has received the most attention; in 1954 when the State Inspection for Protection of Waters was created, all matters in this field were organized under this administrational activity.

This step was necessary to secure the water economy balance in the country.

The quality of our water is of fundamental importance in view of the increasing need for an adequate supply of quality waters requested by the population, industry, and agriculture because our water resources are limited and unevenly distributed over the country. The seasonal water quantity fluctuations are also of importance.

ORGANIZATION OF STATE ADMINISTRATION IN ENVIRONMENT PROTECTION

The water protection problems are centrally supervised and implemented by the Department of Environment Protection in the Ministry of Administration, Local Economy, and Environment Protection. This Department is coordinating and directing the entire activity in this range.

Across the country, the water protection problems against pollutants are regulated and directed by competent divisions of voivodship offices. These divisions are composed of research and testing centers that direct such activities as laboratory tests on the quality of waters and sewages.

THE LEGAL PRINCIPLES FOR PROTECTION OF WATER AGAINST POLLUTION

The Water Act and executional decrees based on it determine the legal principles for activities involved in protecting waters against pollution and those governing the rights and duties of water users. These regulations specify, for instance, the admissible pollution limits for water and the conditions under which sewage and effluents have to be discharged to waters, deep soils, and urban sewage facilities. At the same time, they specify the principles of pecuniary penalties for noxious pollution of waters and how these penalities are to be assessed.

According to the regulations, the waters are noxiously polluted when some physical, chemical, biological, or other changes make them unsuitable for use by the population or by the national economy and when detrimental changes in the environment arise.

The enterprises and plants that drain their sewages into waters, deep soils, or urban sewage facilities are obliged to build suitable sewage purifying plants and to keep them running.

The newly built plants and factories and those that are being enlarged are obliged to start operating such purifying facilities when initiating their production process.

As for the already existing plants without suitable purifying facilities, the Water Act specifies the final time after which they have to be erected and commissioned.

A special water license, issued by a competent regional state administration organization, must be obtained to discharge sewage into waters, deep soils, or urban facilities.

Those who violate the regulations concerning sewage discharges are punished.

The Water Act regulations have introduced the principle of paying for water extraction and for discharging sewages into waters and deep soils. A base is also created at the same time for special protection of some waters so that no sewages are allowed to be discharged into them; the range and principles of such protection are also defined.

SOURCES OF POLLUTANTS

The surface waters in Poland are polluted mainly by industrial waste discharges and by urban sewage, essentially about 2,800 industrial plants and 600 towns have sewage facilities. The industrial works and plants annually originate about 80% of the total volume of all sewage and effluents and constitute the principal area of activity for the environmental protection organizations.

The greatest share of water polluters are the towns and industrial plants with the chemical, food, and wood processing industries, as well as those with mining and power.

About 60% of all sewages that need purification are being filtered to various degrees of final effectiveness by existing purifying facilities in the works and towns.

SCIENTIFIC RESEARCH AND TECHNICAL BASE FOR WATER PROTECTION

The details of the scientific research concerned with protecting water against pollution are being managed by specialized institutes of the individual ministries directing the industry and by the Environment Development Institute (EDI), which coordinates environment protection research, as a whole, in Poland.

The coordinational activity of the EDI is concentrated mainly on programs and plans of the individual scientific research units concerned with protecting the environment.

The primary duties of the institutes of specialized branches include developments in the area of purification process technology for pollutants from the individual industrial branches.

The EDI develops the national needs concerning such general problems as determining standards, water quality norms, methods of classifying and estimating water purity, and also the anti-pollution water programs.

Among the achievements concerned with improving the methods and sewage purification facilities and with developing as well as introducing new purification technologies, the following are significant:

—improved methods and equipment for recovering phenols in sewages and improved methods of biological and physicochemical purification of phenol-laden sewages, up to high limits of purity,

—development and introduction of procedures for biological purification of sewages and effluents resulting from the production of cellulose sulphate,

—development of thermic and hydrothermic methods for treating salinated waters from mines,

—development and introduction of procedures for purifying dairy effluents in biological lagoons,

—development and introduction of procedures for eliminating hydrogen sulphide from waters collecting in sulphur mines.

TRENDS OF FUTURE RESEARCH

The wide development of water protection research work and the practical use of the positive results are guaranteed as a result of our Government's including water resources utilization and development problems into the group of State's problems to be solved gradually by the year 1985.

In the water quality improvement program, which is already accepted, the following research items are included:

—starting the production of test pilot equipment and facilities for sewage treatment and purification,

—optimizing water and sewage economy in the industrial works and enterprises (by applying the closed, no-sewage, and low-water-level circulation systems in the production process),

—developing process technology for producing biodegradable pesticides, detergents, and other chemical products used for agriculture, industrial, and domestic purposes,

—developing highly effective technological processes for treating sewage and for neutralizing sewage sediments, for purifying water, and for reusing water from sewage as well as for desalting the water from mines,

—developing industrial methods of erecting sewage treatment plants, water intakes, and purification and pump-over stations,

—developing and starting continuous data measuring, transmitting, and processing equipment needed for the economy as well as for control of the water purification and sewage treatment stations,

—building a system of measuring and signalling apparatus for weather forecasting service as well as for monitoring the quality of surface water,

—organizing the information needs for the entire country concerned with saving both the quantity and quality of water.

The above all-inclusive program will be determinative in planning the work to be implemented according to the nearest 5-year plans by the individual branch ministries and by the EDI—as the nation-wide coordinator of research in this area—as well as by the technical base centers. Among these centers, a leader in the production of water protection equipment is the Communal Economy Technical Base Union in Poznán, being subordinated to the Ministry of Administration, Local Economy and Environment Protection. The said Union is supervising the "PoWoGaz" Multiplant Enterprise, which includes the Communal Apparatuses and Equipment Factories at Poznán, Pniewo, and Piła. Among other items, production of a small "Biblok" type sewage treatment facility has been commissioned already. Each of these facilities is intended for complete biological treatment of sewage at an output of 100 to 800 m^3/day. They can be utilized especially in small settlements, schools, hospitals, hotels, motels, recreational centers and houses, social facility objects for working teams in industry, and others.

Sewage is treated here according to the low-loaded active sediment method.

A further development of this production in Poland is connected with the possibility of fulfilling the needs that follow from implementing planned recreational and tourist facilities and from the program of providing the small settlements and villages with sewage facilities.

Moreover, the "PoWoGaz" is specializing in the production of:

—measuring and testing apparatuses and equipment for water purification,

—measuring and testing apparatuses for sewage treatment purposes,

—communal services fee meters and some other ones.

REQUIREMENTS AND NEEDS IN SEWAGE TREATMENT

According to assumptions from prospective water protection programs in Poland, repurifying wastewater to a state that fully meets consumer requirements should be reached by approximately 1990. These assumptions are based on knowing the tasks to be carried out during the next 15 years. These tasks will be implemented by:

—equipping all pollutant sources with suitably efficient sewage treatment facilities, according to obligatory legal principles and regulations,

—introducing an accurate water savings regime in industry,

—correctly using newly built sewage treatment plants.

To implement the above, many billions of zloties need to be invested.

Of special importance is the problem of preparing highly effective, technological methodology that has already been confirmed and proven in sewage treatment practice.

When the prognosis for water purity confronts the assumed spacial and economic development of our country in the next 15 years, it can be stated that—especially in the case of some rivers and some of their parts—achieving the required water purity may be impossible with the use of conventional mechano-biological facilities—facilities that limit reduction of pollutants to about 90%. Consequently, further development will have to consider using physico-chemical processes and methods that ensure the possibility of a high-level neutralization of the refractory substances, i.e., those that are processed with tertiary sewage treatment and those in water reuse processes.

Such attitude is justified by the need to take into account, at higher and higher process levels, such pollution factors as: biogenic substances, surface active compounds, pesticides, fertilizers and some other specific ones that after some time will become a limiting factor in water utilization possibilities for the economy purposes. Research institutions are developing adaptations of some of the mentioned processes. Some methods have already been introduced into the process technology, e.g., the distillation process that the Chief Mining Institute used when developing the thermal desalting method in the case of concentrated brines. This method was first tested at a pilot scale in the Hard Coal Mine "Debieńsko" in the experimental plant and, then, in the first newly built desalting plant with a capacity reaching about 270 tons of salt per 24 hr.

Experiments are also being carried out using the reverse osmosis and electrodialysis processes to reduce the mean level of salt waters.

Although a number of treatment plants based on the chemical precipitation processes are already operating, they are not in a sufficient number to meet the country's needs—especially where the treated sewage is discharged into rivers or other open waters used by the local population for a variety of purposes.

Applications of the sorption and ionic exchange processes are also being developed.

Commitments flowing from the international cooperation and especially from the cooperative role of Poland among the Baltic Sea states have been implemented with the use of highly effective methods.

The convention signed in Helsinki in 1974 protecting the Baltic Sea environment aims to limit or to eliminate dumping several pollutants into this sea because they are noxious substances, such as heavy metals (among them, mercury and cadmium), phenols and their derivatives, biogenic compounds, multi-ring aromatic hydrocarbons, oils and petrochemical industry wastes, as well as many other ones that must be eliminated from sewage at high levels of effectiveness.

To ensure the implementation of the commitments following from resolutions of this convention, especially those that

—eliminate or reduce considerably the direct or indirect dumping into the sea of substances and materials listed in the convention,

—equip ships with pollutant collectors or purifiers and ports with equipment for receiving and liquidating these pollutants,

—prepare the technological and organizational facilities necessary to eliminate the effects of an accidental pollution of the Baltic Sea,

—enlarge the scientific and research labors connected with protecting the Baltic Sea against pollution,

—adapt the legal regulations to the requirements following from this convention,

a Baltic Sea environmental protection program has been prepared by the Governmental Ensemble; they determined the detailed tasks within the above-stated range for the individual economic and scientific organizations and institutions—tasks that must be implemented within individual planning periods.

The scientific and research tasks for 1976-80 included in the program consist of:

—methods and technology for measuring the pollution,

—specifying the degree the sea, including the bottom sediments, is polluted,

—specifying the degree the living organisms in the sea are contaminated,

—determining the toxicity of chemical substances,

—determining the degree of self-purification of the Baltic Sea waters, as well as

—methods of preventing sea water pollution.

SUPPLEMENT

Some information on the results of the preliminary exploitation in 1975 of the Biological Wastewater Treatment Plant in Czestochowa (Poland). (Warsaw, February 1976.)

The Central Waste Water Treatment Plant in Czestochowa has been constructed for combined treatment of industrial and community effluents. The stipulated flow capacity of the plant amounts to 160,000 m^3/day. The present volume of wastewater amounts to 80,000 m^3/day.

Industrial effluents make up 50% of the total volume of wastewater inflow. These effluents originate mainly from the following industries: iron and steel, textile, paper, metallurgical, matchmaking, chemical, dyeing, tanning, and food.

The load measured in kilograms per day of pollutants contained in the wastewater inflow is: BOD, 31,500; suspended solids, 41,830; grease, 6,500; sulphides, 95; vol. phenols, 2,400; cyanides, 60; chromium, 2.5; rhodanates, 500; copper, 12; zinc, 6; and lead, 2.

When wastewater containing the above load of pollutants receives preliminary treatment, the quantity of sludge created averages 420 m^3/day.

The sludge is digested by using an anaerobic mesophilic digestion process in separate sludge digestion chambers. The quantity of sewage gas averages 400 to 600 1/kg of dry organic substance.

According to data presented in technical publications, the quantity of sewage gas received from sewage sludge amounts to 470 to 600 1/kg dry organic substance (Imhoff) and to 5 to 25 1/inh. day (Cywinski et al., collected work).

According to the design of the Central Waste Water Treatment Plant in Czestochowa, the excess activated sludge was to be brought into the distribution chamber and then, together with the raw sewage, be introduced into the primary settling tanks. During the preliminary operation of the plant, it appeared, however, that large quantities of excess sludge flowed over the overfalls of the settling tanks and got into the aeration tanks, where it had a negative effect on the process.

Because of this, experiments on separate thickening of the excess sludge in one of the primary settling tanks were carried out with good results. The sludge settled very easily and had good physical and chemical properties (pH, 7.1 to 7.3; organic substance, 70% to 73%; water, 97% to 98%).

To compare, the characteristics of the raw sludge were: pH, 6.0 to 6.3; organic substance, 64% to 68%; water, 93% to 97%.

To choose the most effective and economic system for aerating wastewater, three kinds of aeration systems were investigated: INKA, Kessener, and surface aerator (diam. 2,300 mm, model produced in Poland by PoWoGaz).

The most useful for specific conditions at the Czestochowa treatment plant appeared to be the PoWoGaz surface aerator. Characteristic of the turbine: AP, 2300m; immersion depth of the rotor 5 to 15 cm; OC kg O_2/h, 41 to 75; E_B kg O_2/kWh, 1.6 to 1.7.

Treating the sludge in closed digestion chambers with the use of the I-stage and II-stage processes was investigated. From the achieved results, the II-stage system was recognized as being more useful and effective. The degree of decomposition of organic substances after the I-stage process was about 40% and after the II-stage process was about 50% to 58%.

TRENDS IN SLUDGE TREATMENT AND DISPOSAL PRACTICES IN THE UNITED STATES

Joseph B. Farrell

ABSTRACT

Traditionally, wastewater sludge disposal practice has been decided by location and local circumstance. An overriding consideration has been cost. Ecological factors are now assuming their rightful influence. Serious attention to ecological considerations will cause substantial change in the practice of sludge disposal.

Ocean disposal may be eliminated or, at the least, sludge will be processed to remove harmful materials. New incineration facilities will be obliged to use sophisticated emission controls. If sludge is applied to agricultural land, users must control pathogenic organism and must limit the dose of certain metals to the soil.

New sludge disposal methods being developed are composting sludge with woodchips to make a high quality compost, coincineration with solid waste, pyrolysis, and copyrolysis with solid waste.

Disposal methods that conserve resources would see more application if there were incentives to encourage their use. Similarly, all means of disposal would see improvement if there were adequate standards for measuring performance. Development of incentives and standards will improve quality of sludge disposal.

INTRODUCTION

The amount of wastewater sludge produced in the United States has naturally kept pace with the expanding practice of wastewater treatment. However, when compared with the advances in the technology of wastewater treatment, the technology of sludge disposal has lagged behind. Except for the anaerobic digestion process, processes and equipment were "borrowed" from existing technology with little need for innovative thought. The major concern at a wastewater treatment plant was the purification of the wastewater stream; the concentrated wastes produced were an unpleasant nuisance that had to be rendered innocuous and removed from the plant grounds. There were no standards of quality or measures of performance for sludge comparable with those developed for treated wastewater. The result was that the overriding consideration was cost—cheapest was best. Fortunately, the situation is shifting rapidly, aided by an improved understanding of what constitutes satisfactory disposal procedures.

There is no one best way to dispose of wastewater sludge. An excellent procedure in one part of the country may be both too costly and environmentally unacceptable in another. Numerous factors, from geography to local air pollution codes, influence the disposal choice. Major influencing factors and the factors they influence are presented in Table 1. Factors related to site and circumstances have had the greatest impact on choice of disposal method in days past. It is only recently that ecological factors have received the attention they deserve. For example, the proximity of coastal cities to the ocean made ocean disposal their obvious disposal choice. Today, potential ecological damage is urging a reconsideration of this choice.

TABLE 1. INTERACTING INFLUENCES IN CHOICE OF SLUDGE DISPOSAL METHOD

FACTORS INFLUENCED	
PROCESS CONSIDERATIONS	*DISPOSAL CHOICE*
All process steps such as stabilization and dewatering procedures, even including the choice of the wastewater treatment process itself.	Landfill Incineration Land utilization (cropland, reclamation) Useful products (power, fuel, activated carbon) Ocean
INFLUENCING FACTORS	
SITE AND CIRCUMSTANCE RELATED	*ECOLOGICAL CONSIDERATION*
Geography, geology, climate, conditions at the site, sludge composition (metals, pathogens, volatile solids), sludge quantity, sludge type, population density, proportion and type of industry, other societal influences.	Health effects Air standards Water and groundwater standards Food and crop effects Land use

In the last 10 years, the attitude of the Nation toward pollution and quality of life has drastically changed, and this change has been reflected in the laws of the land. Regulatory agencies at the federal, state, and local level are carrying out the requirements of the laws, and an irresistible movement towards an improved environment has commenced. The law and the spirit of the people have produced two major themes that have impacted the treatment and disposal of sludges. The themes are "protection" and "conservation."

PROTECTION AND CONSERVATION

Every disposal choice is touched by our need to protect our ecosystem against possible harm. We are concerned about protecting the ocean from irreversible change. The oceans are the ultimate sink of wastes discharged by communities either directly to the oceans or to rivers that flow into the oceans. Sludges contain the concentrated wastes from wastewater. In many respects, it is incongruous to separate wastewater into a relatively clean water stream and a concentrated waste stream, and then put them both into the ocean.

We need to protect our communities from the results of improper incineration of sludge. Sludges often give off offensive odors, and they contain higher concentrations of certain potentially hazardous substances than other fuels. We must be sure to use suitable procedures that control odors from incinerators and eliminate the discharge of hazardous particulates and ashes.

The public expects protection against hazards from landfilling of sludge. Sludge should not be placed where it can be washed into streams by rainfall or where rainwater can saturate it, drain through it, and contaminate groundwater. The sludge should not be placed where innocent trespassers can be contaminated with it.

Protection against unwise use of sludge as a fertilizer is needed. The metals in sludge can accumulate in certain crops and residual pathogens in the sludge can contaminate low-growing crops; indiscriminate use of sludge in gardens and truck farms presents a hazard if the level of pathogens is not sufficiently reduced.

Conservation of resources must be considered along with protection from potential hazard. Wastewater sludge contains sufficient nitrogen, phosphorus, and organic matter to make it an extremely useful material in many agricultural applications. Applying it to the soil constructively utilizes organic matter that would otherwise be wasted, and reduces the amount of nitrogen and phosphorus fertilizers that have to be manufactured. Resources needed to make these fertilizers are conserved, and the total "earth burden" of nitrogen and phosphorus fertilizers is reduced. It is evident from the foregoing that the use of sludge on land presents hazards that must be measured against benefits, and here the attitudes of protection and conservation come into occasional conflict. Fortunately careful use of sludge for soil amendment purposes can generally be carried out at loading levels to the soil that are economically attractive to the disposer and present no significant hazard to the environment or the ultimate consumer of the crops.

Conservation urges us to reconsider the wasteful use of high-grade fuels to incinerate sewage sludge. Alternative disposal practices are indicated, or else better means of converting the sludge to an innocuous form should be found. The codisposal of sewage sludge by incineration or pyrolysis with solid waste offers potential. The excess fuel value of the solid waste is more than sufficient to make up for the low net fuel value of partially dewatered sludge. The fuel shortage has made solid waste attractive for other uses, for example, as a supplemental fuel for power plants. However, there will be many situations where sewage sludge and solid waste can be disposed of together with a resultant conservation of resources.

EFFORTS AND TRENDS

In many cases, the pressures for improving sludge disposal practices have not yet crystallized into decisions on alternatives. However, the pace is quickening. Positive action is underway, for example, in those cities that utilize ocean disposal. Those coastal communities that have been under pressure to modify the practice of disposing of sludge to the oceans by ocean disposal or by barge have pursued one or all of the following options: demonstrated that the benefits of sludge disposal to the ocean (low cost, addition of nutrients) outweigh possible risks; modified the composition of sludge to meet concentration limitations; and searched for alternative sludge disposal options. Despite clamor from various cities, federal and state regulatory agencies appear to be holding fast to their conclusion that for sludge with composition outside of the limits suggested[1] risk outweighs benefit and sludge should be kept out of the ocean. There have been no reported successes in treating sludge so that it meets standards. Source control to prevent undesired substances from entering the sewers and ending up in the sludge has been suggested, but indications[2] are that this method will not be successful. Most of the cities have settled down to making sincere efforts to examine alternatives. Major evaluations have been made for Boston, New York, and Philadelphia. The Los Angeles-Orange County area and the San Francisco Bay area have studies underway. The Los Angeles-Orange County study is especially ambitious and includes large-scale pilot plant evaluations of alternatives.

The potential for environmental hazard from inadequate practice of incineration of sludge has been addressed by the U.S. Environmental Protection Agency (EPA). Based on an EPA Task Force study[3] and subsequent action by EPA's Office of Air Programs, standards have been set limiting the particulate loading from sludge incinerators[4] and the quantity of mercury emissions.[5] New construction must meet these standards. Ultimately, the Office of Air Programs is expected to set air standards for concentration of hazardous metals in air. This will impact the concentrations of these metals allowed in the stack gases from incinerators. These standards will probably not be set in the near future. When they are, it is likely that requirements can be met by existing gas cleaning technology.

EPA's Office of Solid Waste Management Programs has had for some years an aggressive program for upgrading procedures used in landfills. They recommend using sanitary landfill and prescribe desirable practices[6]. They currently have underway a contract study to compare the composition and quantity of leachate from landfills where sludge was codisposed with solid waste with leachate from landfills where solid waste alone was disposed.

The EPA has attempted to stimulate and encourage interest in conserving what is good in sludge by applying it to the land. In recent years, concern has arisen about use of sludges on agricultural land. Some crops do not have an effective barrier to prevent uptake of certain metals, and too high a concentration of copper, zinc, or manganese can stunt crop growth. Indications are that under practical growing conditions,[7] much higher loadings of sludge than predicted can be tolerated before crop yields are affected. Nevertheless, current EPA research efforts are emphasizing practical demonstrations and procedures for using sludge to reclaim land and grow nonfood-chain crops; whereas, for agricultural land used to grow food crops, research efforts are being concentrated on developing an understanding of factors influencing metal uptake by crops.

Conservation of fuel in incineration is not only a sensible course from a long-range point of view but is becoming a practical necessity in many areas as natural gas supplies are being limited and costs of oil are skyrocketing. Several municipalities plan to incorporate coal or solid waste with their sludge to raise the heating value to the autothermic point.[8] Consulting engineers are now finding that when disposal is to be incineration, pressure filters are more cost-effective than vacuum filters because they produce a cake dry enough for autothermal combustion.

PROMISING NEW DEVELOPMENTS

The U. S. Department of Agriculture's Agricultural Research Service (ARS) has managed to adapt old technology to sludge disposal. Composting of solid waste is well known but has been relatively unsuccessful in the United States. Quantities of solid waste generated in a given area and converted to compost have been too great and have "flooded" the market for compost in the area. Quality of the compost has not been high because of contamination with inerts and plastic. ARS has produced a compost from woodchips and sludge[9] that has a highly acceptable appearance, has some fertilizer value, and, because per capita sludge production is less than one-tenth of per capita production of organic solid wastes, is unlikely to saturate the local market for compost. The most recent compost process developed by ARS[10] is being demonstrated by EPA and Maryland Environmental Services on raw sludge from the Washington, D.C., Blue Plains plant.

Pyrolysis processes are a new development that may see use for sludge disposal. These processes have been developed for solid waste disposal and offer the possibility of producing high grade fuel. Because volume of gases generated per kilogram of waste processed is much less than that for incineration, gas cleaning costs are much reduced. It is possible to include sludge cake in the pyrolysis step. EPA-sponsored studies by the U. S. Bureau of Mines[11] have shown that much the same product distribution is obtained for dried sludge as for solid waste at the same processing conditions. The EPA is supporting tests of Union Carbide's "Purox" pyrolysis system in which solid waste and sludge will be pyrolyzed together.

THE FUTURE

It is anticipated that sludge disposal in the 1980's will be much different from disposal in the 1960's. Ocean disposal will be essentially eliminated or else sludge will be reprocessed to meet concentration limitations for potentially hazardous substances. Conversion processes, wherein sludge is converted to an innocuous form, will be practiced, but instead of incineration alone, coincineration and copyrolysis with solid waste will be practiced. There will be an increased use of sludge on land, particularly by larger cities instead of just by small communities as is practiced today. Landfills will be used less, since nearby sites are continuing to be filled and standards, such as maximum water content of sludge, will become stricter.

It is hoped that incentives for good practice will be developed. Because the sludge being discharged does not have to meet a quality standard, there is little incentive to do the disposal job well. There is always an incentive to do the job cheaply, but without the need to keep product quality high, the net result can be an inadequate disposal operation. Efforts to develop standards for sludge disposal should clearly be made.

Incentives should also be developed to encourage adoption of methods that conserve resources. Consider a community that evaluates use of its sludge to renovate surface-mined land 60 mi (100 km) away and finds that it is more expensive than destroying the sludge by incineration. The community has no incentive outside of sheer altruism to adopt the course of conservation. This deficiency should be considered by policymakers and lawmakers for correction.

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COMPOSTING OF SEWAGE SLUDGE AND SOLID WASTES MATTER

Józef Cebula

ABSTRACT

The studies on joint composting of sludges and wastes were carried out in connection with the needs of the combined treatment plant in Gluszyca, which serves to protect the Upper Bystrzyca River from pollution. The river catchment area contains a water supply reservoir and, in addition, is of high touristic and recreational value. For these reasons the region is particularly protected.[*] *The sludge from the treatment plant consists of a mixture of industrial and technological sludges. Fifty percent of the sewage comes from textile and tannery industry while the remaining is of communal origin. The sludge contains low concentrations of organic matter and other components essential from the point of view of biological processes and fertilizing properties (CHN and NPKC a).*

The effect of textile and chemical sludges became apparent during the course of studies concerning the possibility of joint composting. The amount of wastes collected in the catchment area was measured directly. Classification analysis of wastes was made, their physicochemical composition was determined, and fractions suitable for composting were selected.

On a dry-weight basis, the concentration of individual components of the wastes, particularly of the organic matter was: RSO, 14%; carbon, 40%; nitrogen, 0.7%; and phosphorus, 0.3%. The values for Ca, N, and K were lower than those found in wastes from large cities.

Plastic baskets with perforated walls were used in the composting experiments, and several series, with increasing percentage of sewage sludges from 0 to 10%, were run. Before composting, the sludge had a greasy consistency, was difficult to dewater, and emitted a putrid odor. In comparison, the sludge compost had the structure, appearance, and odor of fertile soil. The compost was not sticky and was easy to apply on the soil. The compost was found to stimulate plant growth, as measured by the increase of fresh and dry weight and the length of leaves. After analyzing the *results, a 6% to 8% sludge content and 10 t/ha dose were selected as optimum. The presence of the following trace elements in composts and their effects on the growth and composition of test plants were also investigated: arsenic (As), chromium (Cr), tin (Sn), zinc (Zn), cadmium (Cd), cobalt (Co), manganese (Mn), copper (Cu), nickel (Ni), lead (Pb), mercury (Hg), selenium (Se), silver (Ag), and vanadium (V). Mathematical statistics were used to determine the distribution of trace element occurrences in the compost and to determine the reliability of the results obtained. Comprehensive presentation of trace element distribution for individual samples and a comparison of such diagrams allowed the conclusion to be drawn that there is some regularity of trace element occurrence designated as "trace element occurrence periodicity."*

The variability of occurrence periodicity resulting from the varying charge of trace elements can be treated as a technological parameter, which is useful in the determination of sludge suitability for agricultural disposal. This parameter is useful also to determine the potential toxicity of soil under consideration.

The studies demonstrated that it is technologically feasible to dispose of industrial sewage and that industrial composts are suitable for agricultural utilization. It was also recognized that the presence of trace elements in sludges or composts should be used as a principal criterion of the suitability of these materials in agricultural utilization.

INTRODUCTION

Except for occasional cases of industrial waste waters, sewage poses no technical or technological problems. On the other hand, sewage sludges and solid wastes are becoming more and more dangerous as sources of environmental contamination, and only a few rational solutions of sludge and waste management practices are known to eliminate these sources of contamination.[7,8,28] This is particularly true for sludges of industrial origin because their increasing amounts make the disposal problem increasingly difficult. For the most part they contain a significant load of toxic chemicals which are potentially dangerous for the environment. For this reason the possibilities of sludge disposal on cultivated land become limited. These chemicals also include trace elements (heavy metals), which have not been extensively analyzed so far from the point of view of their environmental effects.

In most cases such sludges are disposed of on dumping sites without being dewatered or are stored in lagoons or on waste lands where they accumulate and seriously contaminate soil, ground and surface waters, and air.

Solid wastes are similarly managed by being dumped in various uncontrolled sites, and the use of sanitary landfills is encountered only sporadically.[26,27] In specially protected areas* the elimination of these contamination sources becomes a necessity. It is thus necessary to abandon the traditional methods and to apply newer but, unfortunately, more expensive methods of treating and disposing of sludges and wastes.

It has been found that under some conditions it is possible and advantageous to treat sludges by composting them with solid wastes.[18,19] This procedure produces a much better humus fertilizer than the composting of solid wastes alone, and total costs are lower. Joint composting is also advantageous from the hygienic point of view, because this process totally destroys pathogenic bacteria and weed seeds present in sewage sludge.

So far the practice of joint composting has been based mainly on combining household solid wastes with typical communal sludges.[1,11,4,5] It has been found, however, that it is possible also to compost solid wastes with sludges of industrial origin[3,6,18,19,22] and obtain an "industrial compost" as the final product. Successful final disposal of such compost has become possible by methods developed in the course of studies carried out especially for this purpose. These methods include the utilization of compost to recultivate parks and sport areas, stabilize slopes, waste heaps, high road and railroad embankments, and recultivate dumping sites. Under some conditions it is possible also to use such composts to recultivate forests.[19,20]

Such joint treatment provides some technological advantages and makes possible also a complex solution of sludge and waste management.[8]

A selection and determination of technical and technological conditions of correct solutions depend not only upon the character and composition of both components but also on other factors. These include the kind and character of the protected area, degree of environmental contamination, population density, climate, and technical advancement of the country under consideration.

The Upper Bystrzyca River catchment area was selected for study because it contains the municipal water reservoir Lubachow, which has a high recreational value and is, therefore, especially protected. The protection includes properly managing the sludge and wastes discharged from the combined chemical and biological treatment plant "Bystrzyca." Fifty percent of the sewage is derived from textile and tannery industries and the remaining 50% is of municipal origin.

The excess of industrial and chemical sludges renders biological treatment (methane fermentation or oxygen stabilization) impossible. The sludges are thickened and dewatered mechanically on vacuum filters. Studies concerned with their final disposal and utilization are the subject of this paper.

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*The specially protected regions include the catchment areas of natural and artificial water reservoirs, water intake areas of large cities, regions of recreational value, and national parks.

Taking advantage of local terrain features and considering environmental demands, it was decided to treat the sludge and solid wastes by joint composting, followed by agricultural utilization. Figure 1 shows the kind and extent of the experimental studies performed. The studies were divided into six research topics:

- —the treatment and preparation of sewage sludges for final disposal;
- —the characteristics of household wastes accumulated in the catchment area;
- —the joint composting of wastes with sludge;
- —vegetation studies;
- —the role and effects on soils and plants of trace elements (heavy metals) present in composts; and
- —the practical aspects of sludge compost utilization (one small-scale experiment with positive result).

RESULTS AND DISCUSSION

Sewage sludge treatment and preparation for composting

After being thickened and dewatered on vacuum filters, the sludges were fully analyzed as to their composition, including their nutrient components. The values for the main components, which characterize the physico-chemical composition, differ from those typical of communal sludges. They contain less organic matter and fewer components essential from the point of view of fertilizing and biological properties (C,H,N,P,K,Ca); see Figure 2. The pH is neutral in spite of the high alkalinity of tannery sludge (pH 12).

Characteristics of household solid wastes collected

The interest in this contamination source resulted from the conceived idea of its common treatment with sludges. The studies included:

- —direct determination of the amount of collected waste, mainly because of the volume mixing coefficient;
- —classifying analysis of wastes and determination of physico-chemical composition;
- —selection of waste fractions for composting; and
- —determination of waste particle size.

As a result of these studies, it was established that the coarse and medium fractions can be used in composting. These fractions amount to about 61% of waste weight and contain the majority of organic matter suitable for composting. The composition of wastes differed from the values quoted in the literature. The concentrations of individual components were lower but typical of

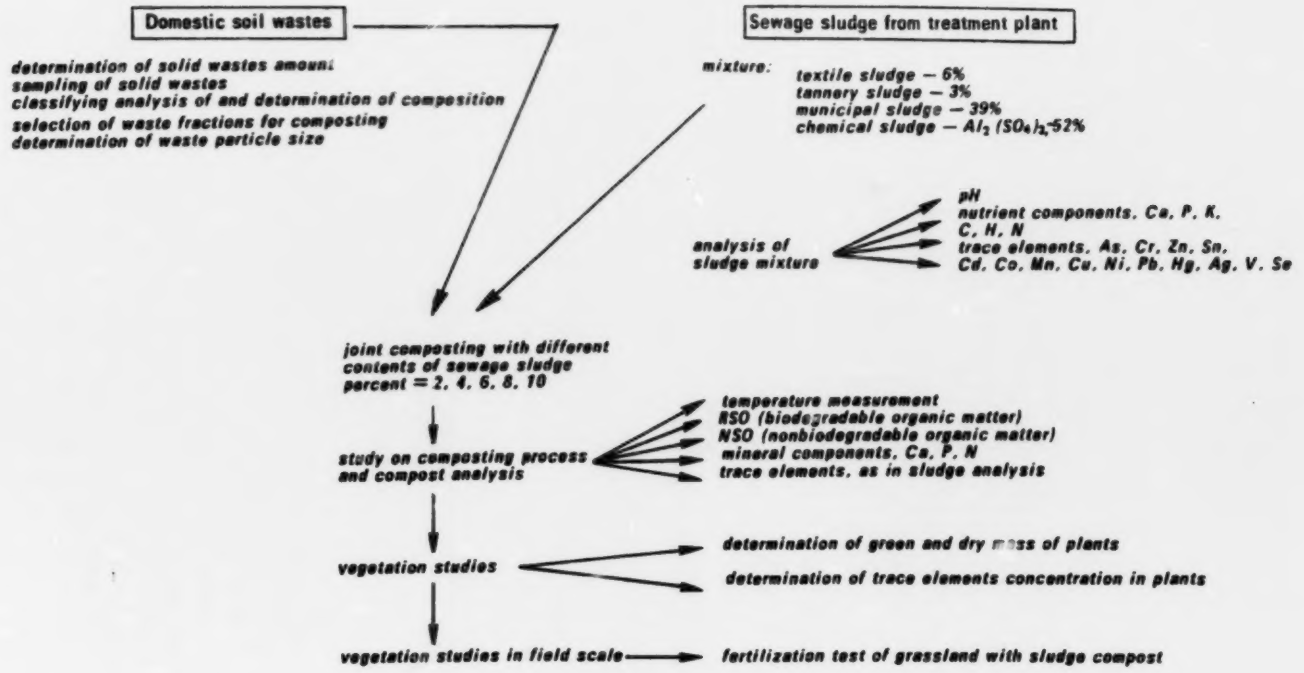
Domestic soil wastes
determination of solid wastes amount
sampling of solid wastes
classifying analysis of and determination of composition
selection of waste fractions for composting
determination of waste particle size
Sewage sludge from treatment plant
mixture:
textile sludge — 6%
tannery sludge — 3%
municipal sludge — 39%
chemical sludge — $Al_2(SO_4)_3$–52%
analysis of sludge mixture
pH
nutrient components, Ca, P, K,
C, H, N
trace elements, As, Cr, Zn, Sn,
Cd, Co, Mn, Cu, Ni, Pb, Hg, Ag, V, Se
joint composting with different contents of sewage sludge percent = 2, 4, 6, 8, 10
study on composting process and compost analysis
temperature measurement
RSO (biodegradable organic matter)
NSO (nonbiodegradable organic matter)
mineral components, Ca, P, N
trace elements, as in sludge analysis
vegetation studies
determination of green and dry mass of plants
determination of trace elements concentration in plants
vegetation studies in field scale
fertilization test of grassland with sludge compost

Figure 1. Kind and extent of experimental studies.

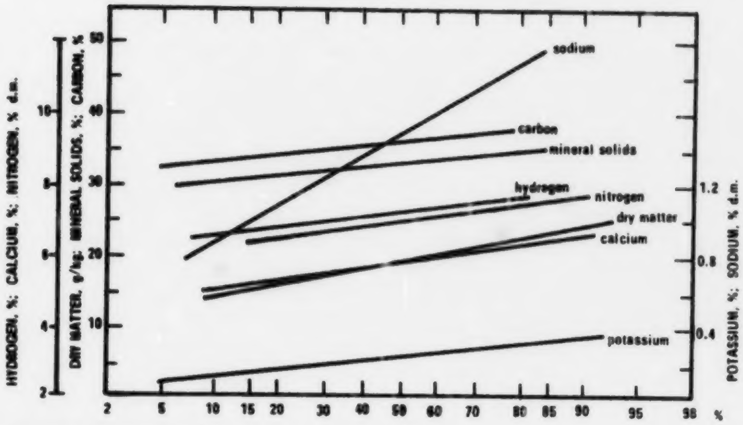

Figure 2. Contamination indices of sewage sludges.

TABLE 1. PHYSICO-CHEMICAL CHARACTERISTICS OF CRUDE COMPOST

No.	Characteristic	Units	Sludge content as dry weight percent of compost					
			0	2	4	6	8	10
1	Organic matter	% s.m.*	44.2	51.5	52.3	44.7	39.4	40.7
2	Biodegradable organic matter	% s.m.	13.6	14.3	13.7	18.6	18.6	19.8
3	Nonbiodegradable organic matter	% s.m.	30.6	37.2	38.6	26.1	20.8	20.9
4	Total nitrogen	% s.m.	0.66	0.63	1.00	0.95	0.93	0.93
5	Total phosphorus	% s.m.	0.26	0.26	0.30	0.23	0.31	0.32
6	Total carbon	% s.m.	43.0	41.0	40.0	38.5	38.8	—
7	C/N ratio		65.2	65.1	40.0	40.5	41.7	—
8	pH		8.7	9.0	8.8	8.4	8.5	8.5
9	Moisture	% s.m.	50.0	50.0	50.0	50.0	50.0	50.0
10	Calcium	mg/g	21.3	14.9	16.3	26.0	21.0	—
11	Sodium	mg/g	0.71	0.35	0.60	1.8	1.20	—
12	Potassium	mg/g	3.48	1.95	3.00	3.0	3.92	—

*% s.m. means % dry weight.

wastes from small communities in Poland. The biodegradable organic matter (RSO) content was 14%; carbon, 40%; nitrogen, 0.7%; and phosphorus, 0.3%. The values of Ca, Na, and K were lower (Table 1). The per head index of waste accumulation in small communities was determined to vary from 0.25 to 0.40 m^3/yr.

Attempts at joint composting of sludges and wastes

Previous attempts at joint treatment were based mainly on combining household solid wastes with typically communal sludges. In previous and present studies, it was demonstrated, however, that it is possible also to compost sludges of industrial origin with solid wastes. In this case, the sludges are not fully neutralized biologically. The process has been termed "biological masking" of industrial sludges with solid waste compost. However, such a procedure yields a harmless product, satisfying from the hygienic and aestetic point of view in comparison with crude sludge or wastes.

The composting experiments were carried out using plastic baskets with perforated walls to ensure good aeration of the material being composted. Several experimental series were performed in which the content of the sludge varied from 0% to 10%. The volume coefficient of sludge and waste mixing will be within these limits in technical scale process. The results of test experiments demonstrated that the composting of sludges from the "Bystrzyca" treatment plant is technologically and technically feasible.

Before being composted, the sludges were greasy, were difficult to dewater, and had a strongly putrid odor. On the other hand, the sludge compost had the structure, appearance, and smell of fertile soil. It was not sticky and was easy to apply on fields (Table 2).

Pilot vegetation studies

The purpose of these studies was to establish if sludge composts had any negative effects on the growth and behavior of plants.

In these studies, the pot tests, adapted to the conditions and purpose of experiments, were used. The growth and development of test plants were observed under constant environmental conditions, i.e. at constant temperature, moisture, and illumination. After 21 days, the increase of fresh and dry weight, leaf elongation, and the number of germinating seeds were measured. These indices were measured at different compost doses.

The sludge compost had a stimulating effect on the increase of the measured parameters, but it was also essential to determine the effect of varying the percent content of sludge in compost (Figure 3). At 2% to 6%, crop yields were higher than those obtained when sludge alone or with compost made of wastes only were used. At a 10% sludge content, the crop yield dropped even below the level of the control experiment.

After the results were analyzed, an optimum percent content of sludges within 6% to 8% and a dose of 10 t/ha were selected. It is assumed that the doses could be higher for grasses because cereal plants are more sensitive to the effects of inhibitory factors.

Negative aspects of agricultural utilization of composts

In addition to the biogenic compounds assimilated by plants, sewage sludges contain chemical substances which may have an adverse effect on plant growth after repeated, prolonged application on soils.[1–3,12,21] Research studies carried out so far were con-

TABLE 2. PHYSICO-CHEMICAL CHARACTERISTIC OF COMPOST AFTER COMPOSTING.

No.	Characteristic	Units	Sludge content as per cent of compost dry weight					
			0	2	4	6	8	10
1	Organic matter	% s.m.*	40.0	46.2	46.3	44.0	38.5	37.7
2	Biodegradable organic matter	% s.m.	10.0	9.6	13.4	15.0	15.1	16.0
3	Non-biodegradable organic matter	% s.m.	30.0	36.6	32.9	29.0	23.4	21.7
4	Total nitrogen	% s.m.	0.76	0.63	0.65	0.93	0.88	0.85
5	Total phosphorus	% s.m.	0.27	0.24	0.27	0.30	0.33	0.35
6	Total carbon	% s.m.	41.2	37.4	40.6	39.4	38.3	—
7	C/N ratio		54.2	59.4	62.5	42.3	43.5	—
8	pH		8.7	8.8	8.8	8.6	8.7	8.4
9	Moisture	% s.m.	50.0	50.0	50.0	50.0	50.0	50.0
10	Calcium	mg/g	22.7	25.5	29.0	27.1	—	—
11	Sodium	mg/g	1.20	2.2	1.9	1.21	—	—
12	Potassium	mg/g	2.90	2.7	2.0	4.60	—	—

* % s.m. means % dry weight.

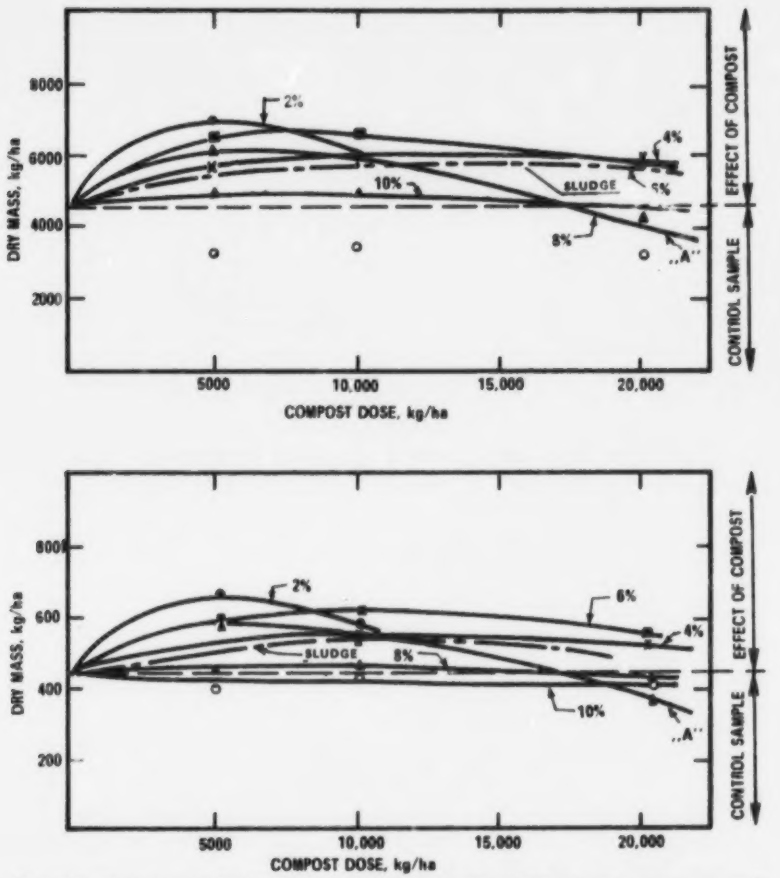

Figure 3. Increase of fresh (top) and dry (bottom) weight of oats grown on soil fertilized with compost from the Bystrzyca River basin.

cerned mainly with the fertilizing value of substances present in sludges and with their effects on crop yields. Only a few studies of the effects of prolonged agricultural sludge utilization have been reported. [9,13] One of the problems resulting from the long-term application of such method of sludge disposal is the accumulation of trace elements up to the toxic levels. [11,15,16]

In discussions concerning environmental quality the term "trace element" is used for substances which, if present in excessive amounts, are toxic for plants, animals, and humans. Under unfavorable environmental conditions and in the case of non-controlled sludge management, the trace elements can lower crop yields or even destroy plants. Trace elements can cause diseases in animals and humans or even death. Such cases are reported in the Japanese and Swedish literature. Lasting destruction of environment can also be due to trace elements. It is clear that this problem should be taken into account when agricultural sludge utilization is planned.[24]

Analyzing only the most important fertilizing substances in the examined composts and observing growth indices are not sufficient to obtain a full evaluation of the usefulness of these substances in agriculture. The experiments performed in numerous research studies indicate that the observed positive effects can be apparent only. The evaluation criteria should be implemented by determination of trace elements concentration in plants.

From the available domestic and world literature, the following trace elements present in higher concentrations in sludges and waste were selected: arsenic, chromium, tin, zinc, cadmium, cobalt, manganese, copper, nickel, lead, mercury, selenium, silver, and vanadium.[2,4,10,16,23,25] Their sources of origin were determined in detail and their negative environmental effects were pointed out.

In the course of our studies, an attempt was made to analyze the levels of these elements in sludge composts, and over 200 samples of sludge, wastes, and composts were analyzed. Mathematical statistics was applied to analyze and interpret the results with the main purpose of determining the occurrence distribution of trace elements and to verify the reliability of the results. The results are presented in the probability and log-normal distribution system. The almost linear shape confirms the correctness of distribution and the reliability of results.

Comprehensive presentation of trace element distribution for individual experiments and then a comparison of these diagrams indicate that there is some regularity of trace element occurrence. This regularity was called the periodicity of trace element occurrence (Figure 4).

Value, mg/g	Hg	Cu	Ni	Zn	Mn	Pb	Cr	Co	V	Se	As	Cd	Ag	Sn
mean	0.64	181.83	71.61	579.63	771.60	141.77	92.86	45.79	102.86	27.36	14.74	17.36	1.49	7.47
median	0.60	200.00	65.00	570.00	880.00	160.00	92.00	47.50	97.00	25.00	14.00	15.00	1.50	7.50
standard deviation		210.86	43.11	382.17	346.41	92.07	17.21	13.69	36.54	16.33	6.84	33.41	0.77	6.30

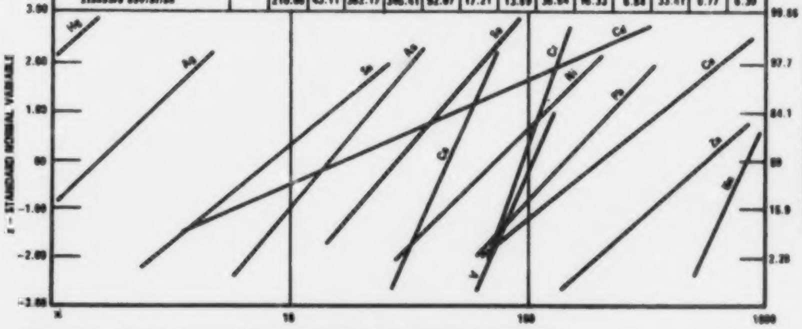

Figure 4. Trace element concentration in sludge composts.

Value, ug/g	Pb	Cu	Zn	Ni	Mn	As	Co	Cr	Sb	Ag	V	Sn
mean	143.00	85.06	193.90	23.24	1017.38	9.80	29.42	94.12	16.23	1.12	73.38	7.80
median	100.00	45.00	105.00	25.00	900.00	11.90	23.00	85.00	17.00	1.00	70.00	7.00
standard deviation	63.95	64.94	61.31	16.32	888.27	7.78	7.83	42.06	8.88	0.31	21.08	3.34

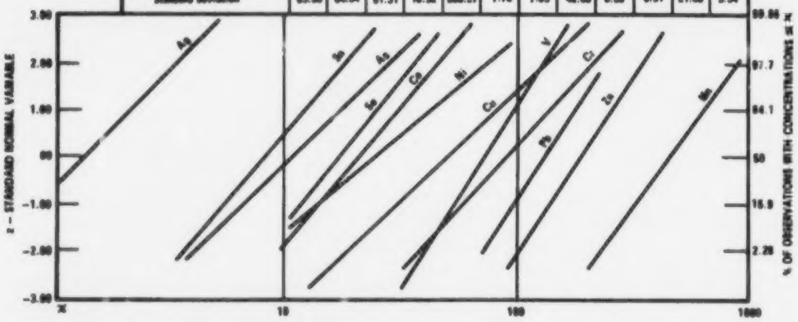

Figure 5. Trace element concentrations in test soil.

Assuming that in soils which were not fertilized with sludges (Figure 5) the occurrence periodicity is natural, the conclusion can be drawn that it may be changed upon application of composts containing a load of trace elements. There will be a moment when the trace element concentration in the soil attains the critical value, and plants begin to assimilate individual elements in larger amounts than required for their growth and development. At this moment (or state) there is a particular periodicity of trace element occurrence. Consecutive shifts in the scale of the diagram, resulting from the impact of the trace elements, can be considered to represent the technological parameter. This parameter determines the usefulness of sludges in agricultural utilization as well as their potential toxicity to an individual soil. This parameter would be, for example, similar to the zinc equivalent.

Our own analytical results are compared with literature data in Table 3. The concentrations of trace elements in the examined sludges and wastes do not differ from values found in sewage sludges from European and American treatment plants. In these countries such levels of trace elements were considered to be alarming and to require action to protect the environment. The character of the Bystrzyca river catchment area has not suggested that such concentrations of trace elements are present in sludges. The increased levels in compost are due, therefore, mainly to the sludges from tannery and textile industry.

Studies of sludge compost effects on plants included the determination of concentration changes of some elements in oats, which were fertilized with various doses of compost having a varying sludge content. However, no essential effect could be observed at the doses applied. This may indicate that the trace element concentrations in sludge compost are still "normal" or that the plant

TABLE 3. A COMPARISON OF AVERAGE TRACE ELEMENT CONCENTRATIONS IN SLUDGE AND SLUDGE COMPOST, ug/g

	Sewage sludges					Solid wastes from	Sludge compost from	
Element	USA	England	Sweden	Poland Lower Silesia	Bystrzyca Treatment Plant	Bystrzyca Treatment Plant	Bystrzyca Treatment Plant	Test soil
Arsenic	7.5	—	—	21	30	19	14.7	9.8
Barium	—	1500	—	—	—	—	—	—
Boron	—	50	—	—	—	—	—	—
Chromium	380	260	86	116	140	103.5	92.1	94.1
Tin	—	120	—	—	—	6.4	7.5	7.9
Zinc	2200	3000	1567	3305	1317	664	579.6	194
Cadmium	12	—	6.7	—	—	4.6	17.3	—
Cobalt	—	12	10.8	27	17	30.8	45.8	20.4
Manganese	—	400	386	416	—	743.5	771.6	1017.3
Copper	700	800	560	163	194	141.2	191.8	55.5
Molybdenum	—	5	—	—	—	—	—	—
Nickel	52	80	51	52	62	83.7	71.6	23.2
Lead	480	700	180	353	337	163.4	141.7	143
Mercury	3.0	20	5.0	—	—	0.4	0.6	—
Selenium	—	—	—	24	97	13.5	27.3	16.2
Silver	—	—	—	—	1.9	4.5	1.5	1.1
Vanadium	—	60	—	54	—	118.3	102.5	73.4

TABLE 4. CONCENTRATIONS OF TRACE ELEMENTS IN TEST PLANTS

Sample	Compost dose kg/ha	Trace element, $\mu g/g$					Type of experiment
		Cu	Ni	Zn	Mn	Fb	
1		30	52	75	75	26	Control test, only test soil
2		50	34	56	43	21	
3		85	42	39	212	17	
4		70	61	70	20	60	
5		11	96	11	11	11	
6	5,000	25	85	25	40	75	Experiment with compost
7		28	100	180	130	174	
8		24	66	19	38	12	
9	10,000	27	17	175	—	—	No sludge, experiment with compost
10		14	14	21	11	87	
11		17	33	17	25	49	
12		18	12	90	23	85	
13	20,000	13	11	26	65	45	
14		51	30	47	13	40	
15		28	55	10	54	54	
16	5,000	21	17	125	—	—	2% sludge, experiment with compost
17		21	17	—	—	—	
18	10,000	54	84	135	32	52	
19		21	17	—	—	—	
20	5,000	22	24	20	13	41	4% sludge, experiment with compost
21		30	63	12	40	10	
22	10,000	50	88	30	55	45	
23		17	15	50	35	12	
24	20,000	9	25	25	12	8	
25	5,000	73	203	20	10	18	6% sludge, experiment with compost
26		20	43	26	20	11	
27		70	20	73	11	27	
28	10,000	55	37	160	92	32	
29		76	40	34	13	40	
30		82	52	11	27	11	
31	20,000	46	23	50	11	29	
32		70	22	49	65	23	
33		23	66	23	11	57	

selected for studies (oats) does not assimilate these elements during its vegetative period (Table 4).

CONCLUSIONS

1. Final disposal of sewage sludges of industrial origin is technologically and technically possible by joint composting with solid wastes. The feasibility of agricultural utilization was demonstrated by the vegetative tests.

2. The uncontrolled disposal of sludges and wastes creates a serious danger for the environment quality, particularly in protected areas.

3. In addition to the main fertilizing components, sludges also contain trace elements which can inhibit plant growth or can be toxic, depending on the kind and concentration of individual elements.

4. The presence of trace elements in sludges and composts should be considered to represent the fundamental criterion of the usefulness of these materials in agricultural final disposal.

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EFFECT OF WATER WORK'S SLUDGE ON WASTEWATER TREATMENT

Janusz Zakrzewski

ABSTRACT

The paper presents results of laboratory research work designed to evaluate the influence of the post-coagulation sludge obtained during water treatment and the filter-washing water (1) on the process and results of municipal sewage treatment and (2) on the process of municipal sludge disposal. The post-coagulation sludge samples have been taken from the Pulsator and from samples of the filter-washing water from rapid filters—all at the Central Warsaw Water Works. Municipal sewage samples have been collected at the Zoliborz-District Pumping Plant, Warsaw.

Results of investigations lead to the following conclusions:

1. *The influence of post-coagulation sludge on the mechanical treatment (primary settling) of municipal sewage is limited.*
2. *The influence of post-coagulation sludge on the biological treatment (activated sludge process) of municipal sewage is limited, too.*
3. *No important difference in total effect of mechanical-biological treatment of municipal sewage should be expected as the result of presence of post-coagulation sludge in raw sewage.*
4. *Although the addition of post-coagulation sludge slightly decreases the effect of thickening and digestion of sludge, it does not influence these processes considerably.*
5. *Further investigation using large-scale equipment should be undertaken to verify the results of these small-scale experiments.*

Notice: The term "post-coagulation sludge" used in the conclusions above means a mixture of the sludge from water coagulation process and filter-washing water mixed in proportions of 1:8.

INTRODUCTION

The combined treatment of municipal sewage and post-coagulation sludge may be considered as one of the methods of sludge neutralization. Polish specialists, as well as specialists of many other countries, have a concern in this method. However, there are serious divergences of opinion on the influence of the aluminium sludge and filter-washing water on the process of municipal sewage treatment and sludge utilization. This is why the investigations in this field have been undertaken in Poland, under the agreement with the United States Environmental Protection Agency, within the Project PR-05-532-7 entitled "Neutralization and Utilization of Post-coagulation Sludge." This paper presents results of laboratory research work conducted by Dr. Jadwiga Bernacka.

THE OBJECTIVE AND SCOPE OF THE INVESTIGATIONS

There were two objectives of this research work: 1) evaluation of the influence of the post-coagulation sludge and filter-washing water on the process and results of municipal sewage treatment; 2) evaluation of the influence of post-coagulation sludge and filter-washing water on the process of the municipal sludge disposal. The term "post-coagulation sludge" in this paper means a mixture of the sludge from the water coagulation process (sludge obtained in Pulsator) and filter-washing water (mixed in proportion 1:8).

The scope of the work in the first objective included the following problems:

- —determining the characteristics of the post-coagulation sludge (the mixture),
- —investigating the influence of the post-coagulation sludge on the sedimentation process of municipal sewage,
- —determining the quantitative and qualitative characteristics of primary sludge obtained as a result of investigations mentioned above,
- —investigating the influence of post-coagulation sludge on the activated sludge process of biological treatment of municipal sewage, and
- —establishing the primary and excess activated sludge balance.

The scope of the work in the field of the second objective included:

- —investigating the ability for gravitational thickening of the primary sludge and excess activated sludge mixture obtained as a result of investigations mentioned above,
- —investigating methane digestion of primary sludge and excess activated sludge mixed in the proportion encountered in conventional wastewater treatment,
- —investigating aerobic stabilization of the excess activated sludge, and
- —testing effect of polyelectrolytes on centrifugation of sludge (effects of shear).

Research Approach

The starting point of the research work was establishing the mixture called here the post-coagulation sludge, e.g. establishing the voluminal proportion of sludge obtained in Pulsator as a result of water coagulation process and filter-wash water. These two ingredients have been mixed in proportion 1:8 (1+7). This proportion has been assessed on the basis of water and sludge quantities produced daily at the Central Warsaw Water Works where samples have been collected.

The water samples were collected each minute of the filter washing period (10 min) and then mixed. The sludge was collected directly from the sedimentation cone of the Pulsator.

Municipal sewage samples were collected at the Zoliborz-District Pumping Plant (Warsaw), where domestic and small-industrial-works sewage are received.

The analysis of post-coagulation sludge included the following: pH value, putrescibility, BOD_5, COD, total dry solids, mineral and organic matter, suspended solids (total, mineral, organic), settleable suspended solids, and aluminium.

The analysis of sewage before and after treatment included the following: pH value, putrescibility, BOD_5, COD, suspended solids (total, mineral, organic), settleable solids.

The analysis of sludge obtained in the sewage treatment process included the following: pH value, dry solids (total, mineral, organic), moisture, CST (capillary suction time). In optimum samples, the ether extract, total nitrogen, and aluminium have been, additionally, determined.

Mixtures of municipal sewage and post-coagulation sludge have been prepared in several voluminal proportions as follows: 100:2; 100:3; 100:5; 100:8. The proportions 100:5 and 100:8 followed the relationship between the quantity of water produced in the Central Warsaw Water Works and the quantity of resulting filter-wash water and Pulsator sludge. Some investigations have been performed to evaluate the influence of Pulsator sludge alone (without mixing with filter-wash water) on the sewage treatment process, applying proportion 100:5. The results of all of these investigations have been compared with the results of municipal sewage treatment process without the post-coagulation sludge (blank run).

DISCUSSION ON THE INVESTIGATION RESULTS

Post-Coagulation Sludge Characteristics

Eighteen (18) samples of post-coagulation sludge have been analyzed, and limit values of results are presented in Table 1. The moisture of sludge was high and significant amounts of mineral compounds were found. The average moisture was 99.93% and the content of mineral matter in dry solids was 73.3%. The content of mineral matter in dissolved fraction and in suspended solids was also high, 69.3% and 75.2%, respectively. The average value of sludge putrescibility was 0.9 hr, which is evidence of its low sta-

TABLE 1. CHARACTERISTICS OF POST-COAGULATION SLUDGE

Characteristic	Units	Values	
		Min.	Max.
pH value	pH	6.2	7.6
Putrescibility	hours	0.4	n.p.*
BOD$_5$	ppm	40	120
COD	ppm	68	640
Total dry solids	ppm	358	1,308
organic	%	18.3	34.5
mineral	%	65.5	81.7
Total dissolved matter	ppm	196	696
organic	%	7.6	44.2
mineral	%	49.5	92.4
Total suspended solids	ppm	122	904
organic	%	18.6	50.5
mineral	%	49.5	81.4
Moisture	%	99.91	99.96
Aluminium	ppm	20	112

*n.p. = not putrescible; did not putrify in the time duration of the test.

bility. The average aluminium content was 54 ppm, which on the average amounted to 7.7% of the dry solids. High variations in BOD$_5$ and COD values were observed (3 to 9 times). The average values of these indicators were BOD$_5$, 80 ppm; and COD, 163 ppm.

Municipal Sewage Characteristics

The results of municipal sewage analyses are presented in Table 2. Composition of municipal sewage samples varied, presumably because of periodic dumping of industrial waste, which was made evident by low pH values, even below pH 4.

TABLE 2. CHARACTERISTICS OF MUNICIPAL SEWAGE

Characteristic	Units	Values		Average
		Min.	Max.	
pH value	pH	3.7	7.5	6.1
Putrescibility	hours	6	n.p.	—
BOD$_5$	ppm	104	353	216
COD	ppm	228	470	329
Total suspended solids	ppm	87	149	117
organic	ppm	55.9	115	87.6
mineral	ppm	19.5	37.3	29.8

The Influence of Post-coagulation Sludge on the Sedimentation Process of Municipal Sewage

The results of investigations in this field can be summarized as follows:

—The addition of the post-coagulation sludge to the municipal sewage slightly increased the effect of mechanical sewage treatment. When the proportion of post-coagulation sludge in sewage was 2%, 3%, or even 5%, its influence on the sedimentation process was insignificant. The influence became well marked when the proportion was 8%. Then the average removal of suspended solids and average reduction of BOD_5 and COD increased 12.4%, 19.9%, and 26.2%, respectively, in relation to the removal and reduction of these indicators in municipal sewage.

—The addition of post-coagulation sludge to municipal sewage at assumed quantities (2% to 8%) caused a slight decrease of BOD_5 and COD values and an increase of total suspended solids in the mixtures, according to the increase of post-coagulation sludge volume in the mixture. The content of organic matter in total suspended solids decreased together with the simultaneous increase of mineral matter.

—When sedimentation time was increased, the effects of treatment increased significantly (BOD_5 and COD reduction, suspended solids removal). As a consequence, the influence of post-coagulation sludge on the mechanical treatment process became smaller.

—The mixtures of post-coagulation sludge and municipal sewage in proportions of 5:100 and 8:100 have been selected as appropriate for the investigations on biological sewage treatment. As stated above, such proportions are compatible with the balance of post-coagulation sludge produced in water treatment plants in relation to water production.

—The addition of post-coagulation sludge caused only a slight increase of aluminium in the mixtures after the sedimentation process.

Primary Sludge Characteristics

During investigation of sedimentation process, sludge obtained after 1, 1½, and 2 hr sedimentation was analyzed, and the increase in sludge volume when post-coagulation sludge was included in the wastewater was observed. This increase was larger as the amount of post-coagulation sludge in the mixture was increased. The concentration of organic matter in dry solids of sludge decreased as the proportion of post-coagulation in the wastewater was increased. The sludge from municipal sewage contained large amounts of grease—on the average 19.4% dry solids. Concentration of grease in mixed samples decreased and was on the average 15.9% (sample 5:100) and 13.4% (sample 8:100). In municipal sludge, the content of aluminium in dry solids of sludge averaged 0.5% and increased to 1.9% in the mixed sample (8:100). The presence of aluminium in municipal sludge was presumably caused by the aluminium contained in the alumino-silicates ordinarily found in soil. The capillary suction time (CST) of sludge was small and decreased slightly in mixed samples.

Influence of the Post-coagulation Sludge on Biological Process of Municipal Sewage Treatment

The parameters of sewage treatment process, using activated sludge, were: capacity of aeration tanks–9 liters each; the aeration time–5 hr; concentration of activated sludge–2,500 to 3,500 ppm; hydraulic loading–4.7 m^3/m^3day; primary sedimentation time –either 0 or 2 hr; secondary sedimentation time–about 2 hr; concentration of dissolved oxygen–about 6 ppm. The results of investigations in this field can be summarized as follows:

—Addition of post-coagulation sludge did not cause any significant change in the qualitative composition of activated sludge microfauna. Some quantitative differences have been observed. It should be stressed that the addition of post-coagulation sludge limited the development of filamentous bacteria. The occurrence of filamentous bacteria in activated sludge affected the floc character of activated sludge. The reticulate structure of sludge caused by the presence of filamentous bacteria in the floc, negatively affected the sedimentation properties of sludge.

—No significant influence of post-coagulation sludge on the process and effects of biological treatment of municipal sewage was observed.

—Activated sludge in tanks supplied with the mixtures of post-coagulation sludge and municipal sewage is essentially the same biotic community familiar to the activated sludge in a tank supplied with municipal sewage only.

—During the whole investigation period, the filamentous bacteria content tended to decrease; this resulted in a decreased sludge index. As the sludge index became lower, the sludge sedimentation properties increased.

—Municipal sewage mixed with post-coagulation sludge can undergo biological treatment without primary sedimentation. With the same aeration time, the results are similar for biological treatment of municipal sewage mixed with the 5% of post-coagulation sludge with or without the primary sedimentation.

The Primary and Excess Activated Sludge Balance

The results of investigations are presented in Table 3.

TABLE 3. EFFECT OF POST-COAGULATION SLUDGE ON TOTAL SLUDGE VOLUME AND MASS

	Municipal sewage	Volume ratio of post-coagulation sludge to wastewater flow	
		5:100	8:100
Volume of primary sludge produced after 2 hr sedimentation	2.9 dm^3/m^3	4.6 dm^3/m^3	5.9 dm^3/m^3
Relation of volume of primary sludge to excess activated sludge	1.3 : 1	1.6 : 1	2.2 : 1
Above, expressed in dry solids	4 : 1	3.8 : 1	2 : 1

Effect of Thickening the Mixture of Primary Sludge and Excess Activated Sludge

The best gravitational thickening effect was achieved by the municipal sludge without post-coagulation sludge. Average solids content of the thickened sludge was 2.66%. Slightly lower degrees of thickening have been gained for the mixtures containing 5% or 8% of post-coagulation sludge; solids contents of the thickened sludge were 2.1 and 1.78, respectively. The lowest degree of thickening (1.35 solids) was for the excess activated sludge containing 5% of post-coagulation sludge but no sludge from the primary clarification.

As the volume of post-coagulation sludge in the mixture increased, the optimum thickening time increased slightly. At the same time, however, the degree of thickening decreased. Capillary suction time of sludge (CST) after thickening increased in accord with the increase in volume of the post-coagulation sludge in the mixture.

Effect of Post-Coagulation Sludge on the Methane Digestion of the Mixture of Primary Sludge and Excess Activated Sludge

Post-coagulation sludge evidently influences the effectiveness of the methane digestion process. The presence of post-coagulation sludge has caused the rate of digestion to decrease. The greater the quantity of post-coagulation sludge in the mixture, the greater the influence; this could be observed by the smaller quantities of gas (methane) generated. With a mixture of 5% of post-coagulation sludge, the average decrease of production of methane was 8%

and with 8% post-coagulation sludge, the decrease was 17.5%. A 21- to 28-day digestion time should be allowed; the effect of a 14-day process might be insufficient. Second stage digestion decreased the water content of the mixed sludge, and the longer the digestion process, the less polluted was the effluent.

Effect of Aerobic Stabilization of the Excess Activated Sludge

The activated sludge (containing post-coagulation sludge) required 14 days for aerobic stabilization. The aerobic stabilization process improved the ability of this sludge to thicken.

CONCLUSION

Results of investigations on the influence of aluminium sludge and filter-wash water on the process of municipal sewage treatment and sludge utilization lead to the following conclusions:

1. The influence of post-coagulation sludge on the process and on the effect of mechanical treatment of municipal sewage is limited.
2. The influence of post-coagulation sludge on the process and effect of biological treatment of municipal sewage is limited, too.
3. No important difference in total effect of mechanical-biological treatment of municipal sewage should be expected because of the presence of post-coagulation sludge in raw sewage.
4. Although adding post-coagulation sludge slightly decreases the effect of thickening and digestion of sludge, it does not influence those processes substantially.
5. Further investigation using large-scale equipment should be undertaken to examine the results of the lab-models work.

PHYSICAL-CHEMICAL TREATMENT OF COMBINED STEEL MUNICIPAL WASTEWATER

Jan Suschka

ABSTRACT

Combined steel and municipal wastewater can be treated effectively using biological methods. However, the removal rate for organic substances seems to be lower than that for municipal sewage. Using physical-chemical treatment does not have an advantage especially when high-quality effluent is required. The investigations carried out indicate that thorough mixing associated with aeration and sedimentation essentially removes pollutants. Adding anaerobic digested sludge further improves the treated wastewater quality. However, more research is needed to evaluate optimal conditions.

THE SCOPE OF THE RESEARCH

Wastewater originating mostly from steel and related industries is characterized by the presence of metals and other substances that can have an inhibitory effect on biological treatment. Investigations on the activated sludge process and trickling filters show a lower kinetic rate of removal of organic substances than that of municipal wastewaters. Probably the most important reasons are the inhibitory substances from industry and the shock loads that can be responsible even for complete destruction of the active biological floc.

Another reasonable approach seems to be physical-chemical treatment, direct or after primary sedimentation. This approach was reported by many authors to be effective when treating wastewaters of low organic content. In contrast with the use of classical coagulants and polyelectrolytes, the possibility of using substitute substances was examined in the scope of this work.

The combined wastewater originating in part from steel mills and metal finishing plants contained relatively high iron concentration. The maximum concentration varied in the range of 70 to 80 mg/l. The average concentration was about 25 mg/l. Sludge from primary or secondary settling tanks is characterized by a concentration of about 200 g Fe/kg of dry matter. It was then suggested that the applicability of sludge derived from different points of the wastewater treatment process be investigated as an aid or single coagulant for wastewater purification.

To get the desired information, laboratory and pilot-scale research was done on the effect of treatment with classical coagulants. Also, research on the activated sludge process, trickling filters, and aerobic and anaerobic stabilization of sludge was done.

WASTEWATER CHARACTERISTIC

The average flow of wastewaters to be treated is about 1.5 m^3/sec. The flow varies during the day from about 1.0 to 1.8m^3/sec. During rainy periods, the flow can increase up to 7 m^3/sec. Many 24-hr samples (hourly composites) of combined wastewater were examined, as were grab samples. Also, before each treatment, the wastewaters were examined. To understand the magnitude of the parameters measured, the average values and the range of pollutant concentration are given (Table 1). The maximum values given in Table 1 do not include the extreme values that can be found only occasionally.

TABLE 1. CHARACTERISTICS OF THE COMBINED WASTEWATERS

Parameter	Average	Minimum	Maximum
pH	7.5	6.9	8.0
Turbidity, mg/l SiO_2	500	100	900
COD, unfiltered, mg/l O_2	240	120	540
COD, filtered, mg/l O_2	150	60	240
BOD_5, mg/l O_2	110	60	145
Suspended solids			
Total, mg/l	190	100	350
Volatile, mg/l	120	60	200
Alkalinity Zm*, mval/l	4.2	3.3	6.4
Zp, mval/l	0	0	0
Calcium, mg/l	125	70	170
Magnesium, mg/l	60	35	95
Sulphates, mg/l	445	230	660
Sulphur total, mg/l	130	85	230
Phenols, mg/l	0.09	0.001	0.2
Cyanides, mg/l	3.5	2.2	4.0
Iron, mg/l	25	6	80
Zinc, mg/l	2.0	0.8	3.2
Lead, mg/l	0.12	0.10	0.15
Copper, mg/l	0.18	0.12	0.30
Ammonia nitrogen, mg/l	32	28	45
Nitrate nitrogen, mg/l	0.8	0.3	4.2

* Alkalinity determined by titration with methyl orange is given as Zm; when phenolphthalein is used as an indicator, Zp is used.

BIOLOGICAL TREATMENT

Activated sludge, which was investigated for detention times of 1.2 and 4 hr, showed the possibility of effectively removing organic substances. Under optimal conditions, decreasing BOD to about 10 mg/l and filtering COD to 40 mg/l was possible.

Similar results were obtained for the trickling filter treatment. After secondary clarification, wastewater turbidity was low (in the range of 30 mg/l) as was the concentration of suspended solids (in the range of 20 mg/l). The quality of biologically treated wastewater was high even with a relatively high load of organic substances (in the range of 0.5 to 1.0 g BOD/g MLVSS per day.

AEROBIC AND ANAEROBIC SLUDGE STABILIZATION

Primary sludge was aerobically stabilized for 10 days. Because of the biooxidation of a part of the organic substances, the relative concentration of inorganic substances increased. The concentration of total iron in relation to dry matter changed slightly during the process—from 16.7% to 16.9% in one run and from 17.6% to 22.8% in the second run. The fractions of VSS after aerobic stabilization were 48.6% and 40.4%, respectively, i.e., 15% lower than at the beginning.

The process of anaerobic stabilization was carried out at a temperature 32°C with detention times of 29 and 36 days. The respective loads were 0.14 and 0.15 kg dry matter/m^3 per day. The gas production was 1.15 m^3/m^3. The iron content in the digested sludge was relatively low (in the range from 7-12%). The process of iron solubilization was observed. In the supernatant, the soluble iron increased from 6 and 12 mg/l to 27 and 46 mg/l, respectively, in two runs.

The aerobic and anaerobic digested sludge as well as the anaerobic supernatant was used to investigate wastewater coagulation.

PHYSICAL-CHEMICAL TREATMENT

The major part of this research was based on jar tests although several series of continuous laboratory and pilot-scale investigations were carried out. Before going into the results of the true coagulation process when ferrous or alum salts or other chemicals were added, it seems to be important to mention the effects of mixing and sedimentation on the wastewater quality.

During the jar-test investigations, it was found that plain 1-min rapid and 20-min slow mixing followed by a 30-min sedimentation time results in distinctive changes in wastewater quality. Because of this simple process, the turbidity decreased on the average, from 500 to 95 mg SiO_2 (in the range of 80%). This was also true of suspended solids removed; the average suspended solids concentration decreased from 190 to 40 mg/l (about 80%). But only a

2% COD removal was obtained from a filtered sample; that, of course, could be expected. The observations made are very important when discussing the problem of physical-chemical treatment of wastewater. They show explicitly how important the primary treatment stage, including mixing, is.

From many experiments it was concluded that primary treatment is best when preaeration process is used. This process, lasting from 10 to 30 minutes, results in thorough mixing and oxygenation. Besides improved removal of suspended solids and turbidity, heavy metals can be removed during the sedimentation process.[1] An example of the effects of preaeration process for removing suspended solids and turbidity is given (Figure 1). It was demonstrated that preaeration removes more turbidity and suspended solids than does plain mixing and sedimentation. Adding lime to raise the pH to 8.5, 9.0, and 9.5 (from 7.4) has little or no advantageous effect (Figure 1).

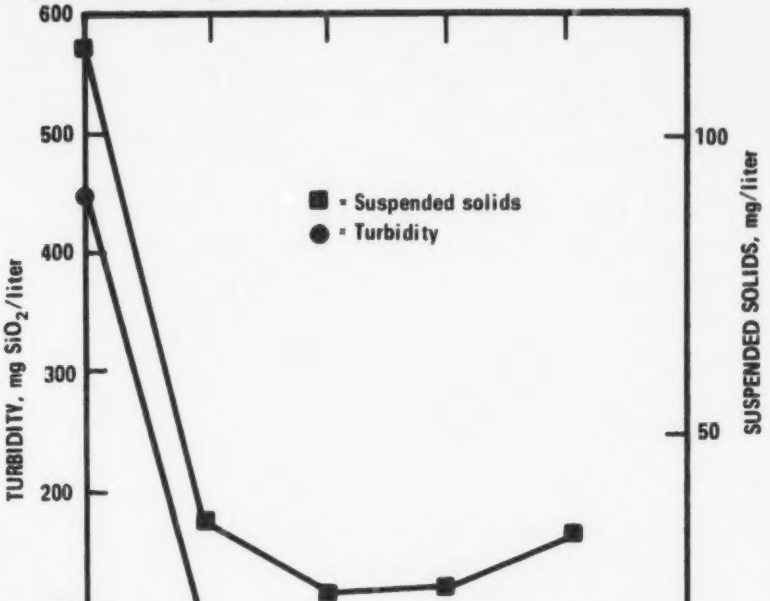


Figure 1. Effect of preaeration on removal of suspended solids and turbidity. Sample 0 involved plain mixing and sedimentation; Sample 1, 30 minutes of preaeration; Sample 2, 30 minutes of preaeration and pH raised to 8.5; Sample 3, 30 minutes of preaeration and pH raised to 9.0.

On the base of many investigations, it was demonstrated that increasing pH through lime addition cannot be justified as a treatment process. From Figures 2, 3, and 4, where the mean values as well as the ranges are given, it is obvious that further distinctive improvements of the wastewater quality can be achieved.

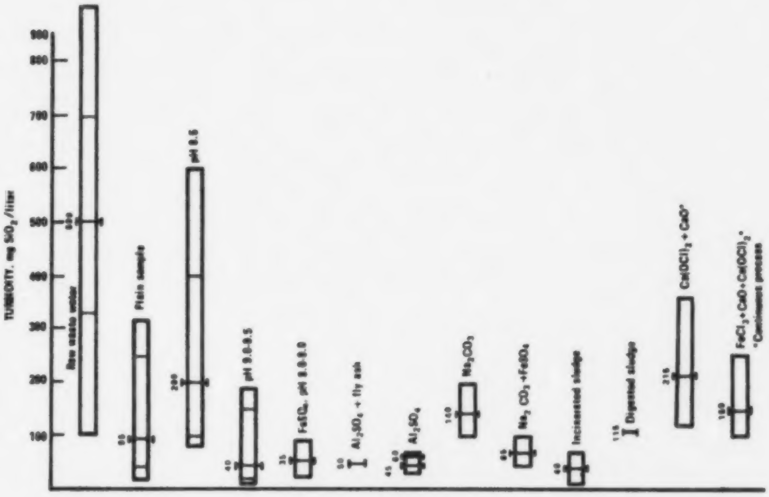


Figure 2. Effect of using different chemicals, substances, or process conditions on turbidity.

Even in the case of suspended solids, an unexpected increase was observed. The turbidity at pH above 9.0 decreased to 40 mg/l, that is, to about 60% of the plain mixing-sedimentation process. Also, a 20% removal effect of COD was obtained by pH increase.

The Figures 2, 3, and 4 comprise also the results of investigation with the use of other classical coagulants. In relation to the scope of this research, it seems to be important to compare the results achieved when using incinerated and anaerobic digested sludge in place of chemicals.

From the results presented in Figure 2, it is evident that the turbidity of wastewaters treated with incinerated sludge is comparable with that obtained at pH 9.5 with the addition of copper or at pH increased to 8.5 and 9.0 with addition of alum.

Similar conclusions can be derived comparing the results of suspended solids and COD removal.

It has to be stressed that similar results for COD removal (in the range of 45% with a remaining value of 60 mg/l) could be obtained only when alum and alum in addition to fly ash was used.

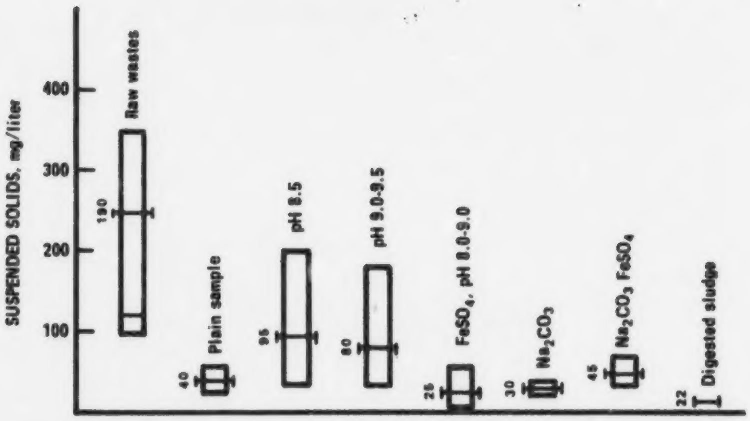


Figure 3. Effect of using different chemicals, substances, or process conditions on suspended solids. Mean value indicated at ——.

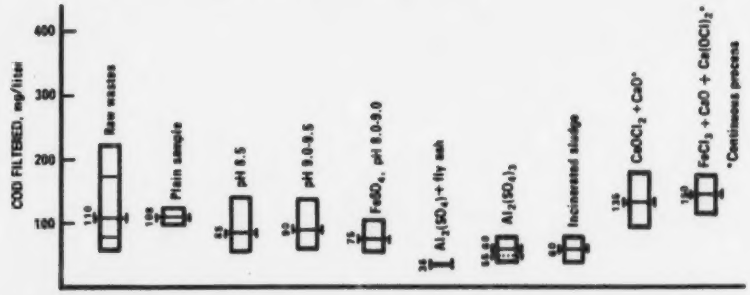


Figure 4. Effect of using different chemicals, substances, or process conditions on COD. Mean value indicated at ——.

Satisfactory coagulation was also obtained when anaerobic digested sludge was used. In Figure 5 are the results obtained with two different doses of anaerobic digested sludge.

With an excellent removal value of as low as 22 mg/l, the conclusion is that the use of sludge as a coagulant or a coagulant aid seems to be very promising. However, it is too early to scale up the results to a full technical scale, for a time limitation allowed only several runs. Also, the use of incinerated sludge was tested during a rainy period of the year and wastewaters were relatively "weak" when compared with the average values.

Treating combined steel/municipal wastewater with physical-chemical methods has no advantage over biological methods; the only justification for using physical-chemical methods is the use of substitute coagulants.

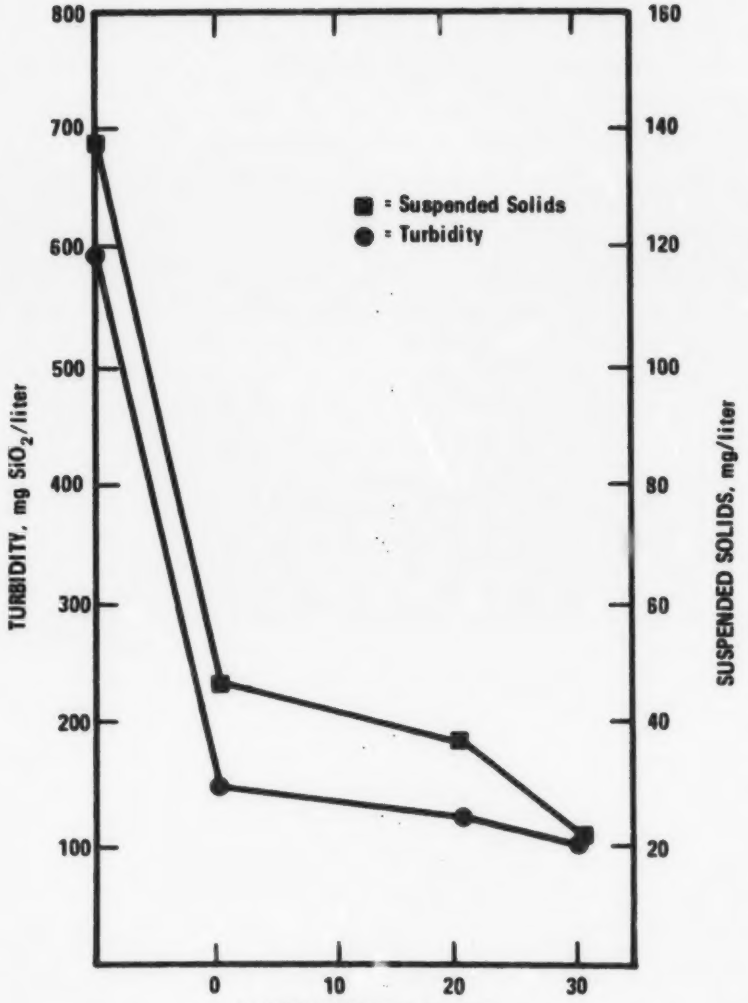


Figure 5. Effect of using anaerobic digested sludge on turbidity and suspended solids.

COMPARISON OF ALTERNATIVE STRATEGIES FOR COKE PLANT WASTEWATER DISPOSAL

Robert W. Dunlap and Francis Clay McMichael

ABSTRACT

Fifty years ago the production of coke from byproduct ovens surpassed the production from beehive ovens. Although oven-coke production has remained stable, chemical recovery has grown increasingly less advantageous. By 1973, coal chemicals amounted to only 12% of total product value. Recently, attention has been focused on another principal difference between byproduct and beehive coking, namely water pollution as a result of gas treatment and byproduct recovery.

In 1974, the U.S. Environmental Protection Agency issued effluent guidelines and standards for iron and steel manufacturing. Limitations were set for oil and grease, suspended solids, pH, and sulfides, but the principal attention for the guidelines was for the control of ammonia, cyanide, and phenols.

This study examined a number of topics related to coke plant wastewater problems. Answers were sought to these questions: What are the specific sources of the wastewaters? Can they be reduced by process changes? How do process changes and wastewater treatment impact air, land, and energy demands?

Seven different wastewater treatment strategies were evaluated considering the mass emission inventory and cross-media analysis. The findings were that wastewater treatment provides environmental improvement for one media, water, but will lead to the degradation of other media, air and land. Energy requirements for treatment processes create new pollutant residuals, which are smeared across all media.

For some wastewater treatment practices, the new environmental improvement due to the practice is negative, i.e., cross-media effects are so large as to negate the beneficial effects of improving the water media. The results of this study clearly support the contention that levels of environmental control must be considered very carefully if maximum improvement of the environment is to take place.

TRENDS IN COKE MAKING

Fifty years ago, the production of coke from byproduct ovens first surpassed the production from beehive ovens. For many of these same years, the byproduct process was praised for two significant advances over beehive coking: first, byproduct processing introduced significant chemical recovery into coke making and second, byproduct processing significantly reduced air pollution problems associated with coking. The last 20 to 25 years, however, have brought a changed perspective. While oven-coke production has remained stable at 54 to 64 million metric tons/yr over the last quarter century, chemical recovery has grown increasingly less advantageous. In 1950, 22% of product values from the coke plant were associated with the value of coal chemicals.[1] By 1973, coal chemicals represented only 12% of total product value. At the same time these changes were taking place, increasing attention has been focused on the other principal difference between byproduct and beehive coking, namely, the introduction of significant water pollution problems which are a direct consequence of the gas processing.

EFFLUENT GUIDELINES

Coke plant effluent limitations have been imposed by the U.S. Environmental Protection Agency (EPA).[2] It is recognized that coke plant wastewaters are typically as saline as sea water and contain a broad range of organics. Limitations are set for oil and grease, suspended solids, pH, and sulfides, but the principal attention for the guidelines are for the control of ammonia, cyanide, and phenolics. By 1977, the guidelines call for more than 90% reduction of these pollutants from the levels in typical untreated process waters. Further control by 1983 is expected to reduce discharges of the three by more than 99% (Table 1).

The intent of this study is to address the coke plant wastewater problem by examining a number of topics. What are the specific sources of the wastewaters? Can they be reduced in quantity

TABLE 1. EFFLUENT LIMITATIONS FOR SELECTED COKE PLANT POLLUTANTS, kg/mil kg coke

Pollutant	Typical raw wastewaters	BPCTCA* 1977	BATEA† 1983
Ammonia	914	91.2	4.2
Cyanide	120	21.9	0.1
Phenol	262	1.5	0.2
Average percent removal	0.0%	91.2%	99.7%

* BPCTCA is "best practicable control technology currently available (other than publicly owned treatment works)."

† BATEA is "best available treatment technology economically achievable."

through process changes? How do process objectives and environmental demands like control of air pollution influence waste characteristics? How can we evaluate the environmental impacts to air, water, and land which result from process effluents or are associated with the energy demands of process control?

COKE PLANT WASTEWATER SOURCES

Byproduct coke plants vary widely in size, extent and type of byproduct recovery, and wastewater practices. Wastewaters in coking originate from three principal sources: coal moisture, water of decomposition, and process waters added during gas treatment and byproduct recovery. The process waters are the largest fraction of the total wastewaters and typically account for 60% to 85% of the total flow, which may range from 500 to 1700 l/metric ton depending on the level of process water recycle. Typical gas processing and recovery steps are shown in Figure 1, which indicates the six categories of wastes normally identified: (1) tar still wastewater, (2) excess or waste ammonia liquor (WAL) from the primary cooler, (3) ammonia absorber and crystallizer blowdown, (4) final cooler wastewater blowdown, (5) light oil (benzol) plant wastewater, (6) gas desulfurizer and cyanide stripper wastewater. Table 2 indicates the level of wastewater flow and mass emissions of cyanide, ammonia, and phenol for each of the waste-

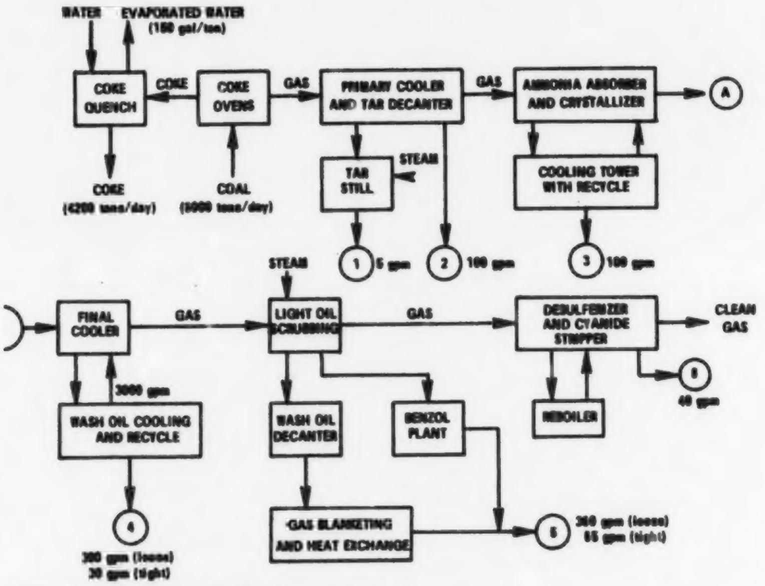

WATER
EVAPORATED WATER (150 gal/ton)
COKE QUENCH
COKE
COKE OVENS
GAS
PRIMARY COOLER AND TAR DECANTER
GAS
AMMONIA ABSORBER AND CRYSTALLIZER
A
COKE (4200 tons/day)
COAL (6000 tons/day)
TAR STILL
STEAM
COOLING TOWER WITH RECYCLE
1
5 gpm
2
100 gpm
3
100 gpm
STEAM
FINAL COOLER
GAS
LIGHT OIL SCRUBBING
GAS
DESULFERIZER AND CYANIDE STRIPPER
CLEAN GAS
3000 gpm
6
40 gpm
WASH OIL COOLING AND RECYCLE
WASH OIL DECANTER
BENZOL PLANT
REBOILER
4
300 gpm (loose)
30 gpm (tight)
GAS BLANKETING AND HEAT EXCHANGE
5
360 gpm (loose)
85 gpm (tight)

Figure 1. Schematic of coke plant wastes.

TABLE 2. CHARACTERISTICS OF COKE PLANT WASTEWATER STREAMS*

Wastewater stream	Flow		Mass flow		
	gpm	lpm	Cyanide, kg/day	Ammonia, kg/day	Phenol, kg/day
Flow with loose recycle:					
1. Tar still	5	20	2	136	132
2. Waste ammonia liquor	100	380	33	3270	794
3. NH_3 crystallizer	100	380	8	6	2
4. Final cooler	300	1140	164	65	63
5. Benzol	360	1360	4	6	10
6. Desulfurizer	40	150	246	0	0
Total	905	3430	457	3483	1001
Flow with tight recycle:					
1. Tar still	5	20	2	136	132
2. Waste ammonia liquor	100	380	33	3270	794
3. NH_3 crystallizer	100	380	8	6	2
4. Final cooler	30	110	82	33	40
5. Benzol	65	250	2	2	3
6. Desulfurizer	40	150	246	0	0
Total	340	1290	373	3447	971

* Basis: 5443 kkg/day coal charged at 10% moisture with 70% coke yield, equivalent to 3810 kkg/day coke product.

water streams. Loose or tight recycle is a measure of the flow reduction achieved through recycle and process modification in the final cooler and the benzol plant. Mass emissions are essentially the same for both configurations with the exception of some loss of pollutants assumed for tight recycle due to byproduct contamination, volatilization to the atmosphere in open cooling towers, and development of corrosion products in the coke oven gas distribution system.

The environmental impact of these wastewater streams can be summed up by considering the overall mass balance of emissions to the air, water, and the land. The coke plant necessarily consists of coke ovens, the quench towers for the incandescent coke, the byproduct plant, and an associated wastewater plant to treat the wastes to meet the guidelines. Figure 2 shows the principal plant input, coal, and the main outputs of coke, coal chemicals, and coke oven gas. The mass balance must also include air emissions from the open cooling tower and the quench tower in the form of volatiles and particulate matter. Water emissions may be adequately represented by ammonia, cyanide, and phenol. To control the wastewater effluents to the degree required by current regulations, a new element must be added—energy in the form of steam and electricity is needed to operate the treatment systems.

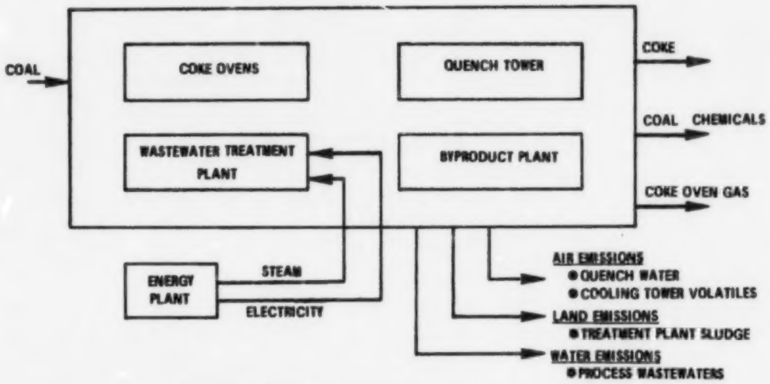

COAL
COKE OVENS
QUENCH TOWER
WASTEWATER TREATMENT PLANT
BYPRODUCT PLANT
COKE
COAL CHEMICALS
COKE OVEN GAS
ENERGY PLANT
STEAM
ELECTRICITY
AIR EMISSIONS
● QUENCH WATER
● COOLING TOWER VOLATILES
LAND EMISSIONS
● TREATMENT PLANT SLUDGE
WATER EMISSIONS
● PROCESS WASTEWATERS

Figure 2. Input and mean outputs of a coke plant.

Energy for Wastewater Control—Alternative Strategies

The energy system is examined more closely in Figure 3. It consists of a power plant, assumed to be a coal-fired boiler, to raise steam and to generate electricity for the wastewater treatment plant. The power plant also produces environmental emissions even though the plant is configured to meet applicable air and water regulations. Particulate matter, sulfur dioxide, nitrogen oxides, and waste heat are emitted to the air. Waste heat goes to the water; land emissions are ash and sulfur dioxide scrubber sludge from the power plant, as well as demineralization or softening sludge from the boiler water treatment plant. An interesting problem now arises. It appears that as one problem is solved–the wastewater effluent problem from the coke plant–another emission problem is created, namely the disposal of effluents produced from generation of the required steam and electricity. Furthermore, it seems obvious that more and more energy will be required as the level of wastewater treatment becomes more stringent. To decrease the effluents from the coke plant, one must increase the effluents from the boiler plant. Several questions are posed. Are we working at cross purposes? What is the net environmental impact? How do we obtain an optimum level of wastewater treatment which achieves the maximum environmental improvement, considering all effects? To answer these questions, it is necessary to perform a careful environmental assessment of the coking operation, including an examination of alternative strategies for handling the wastewaters. Table 3 lists eight alternative strategies (Cases 0 through 7) for controlling wastewater discharges. Each strategy involves one of three levels of wastewater treatment (Raw wastewater, Level I, Level II), one of two levels of recycle (Loose, Tight), and one of two quenching practices (Clean, Wastewater).

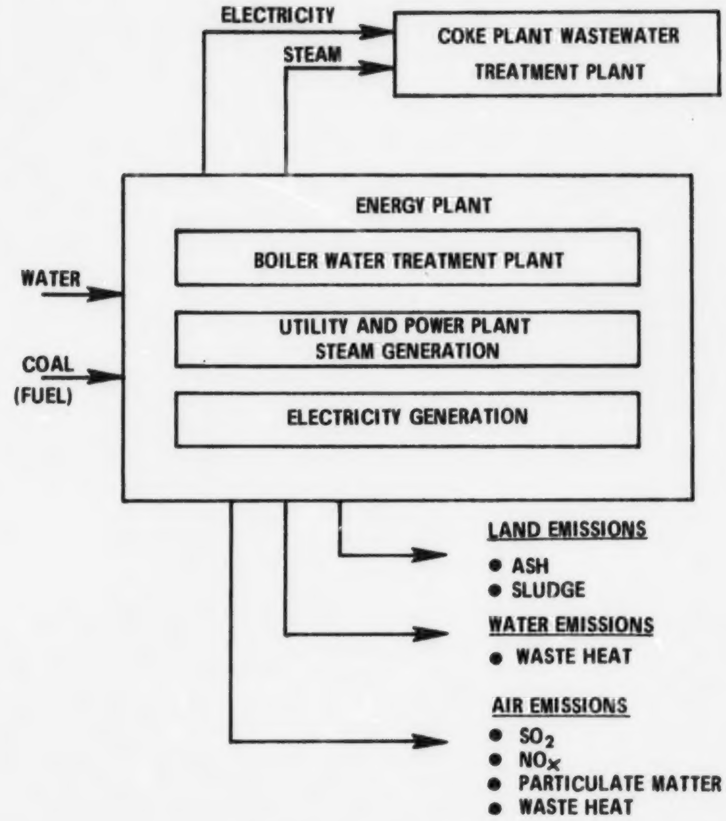

ELECTRICITY
STEAM
COKE PLANT WASTEWATER TREATMENT PLANT
ENERGY PLANT
BOILER WATER TREATMENT PLANT
UTILITY AND POWER PLANT STEAM GENERATION
ELECTRICITY GENERATION
WATER
COAL (FUEL)
LAND EMISSIONS
• ASH
• SLUDGE
WATER EMISSIONS
• WASTE HEAT
AIR EMISSIONS
• SO_2
• NO_x
• PARTICULATE MATTER
• WASTE HEAT

Figure 3. Inputs and outputs of the energy system needed for the coke plant.

TABLE 3. COKE PLANT WASTEWATER CONTROL STRATEGIES

		Level of recycle		Type quench	
Case	Treatment	Loose	Tight	Clean	Wastewater
0	Raw wastewater	X		X	
1	Raw wastewater	X			X
2	Raw wastewater		X	X	
3	Raw wastewater		X		X
4	Level I		X	X	
5	Level I		X		X
6	Level II		X	X	
7	Level II		X		X

Flow processes for the wastewater treatment strategies are shown in Figures 4 and 5 for a hypothetical coke plant configured for this study. The wastewater flows are generated from recovery operations found in many steel plants. With a daily coal charge of 6000 tons (5443 kkg) and a daily furnace coke production of 4200 tons (3810 kkg), such a plant would be among the largest 25 plants in the country. Level I treatment is wholly a physical-chemical system employing a method for cyanide stripping based on existing technology developed by Bethlehem Steel Corporation,[3] ammonia removal using a conventional still, and phenol extraction based on existing technology developed by Jones and Laughlin Steel Corporation.[4] Level II is a higher level of treatment combining physical-chemical operations with biological waste treatment. The

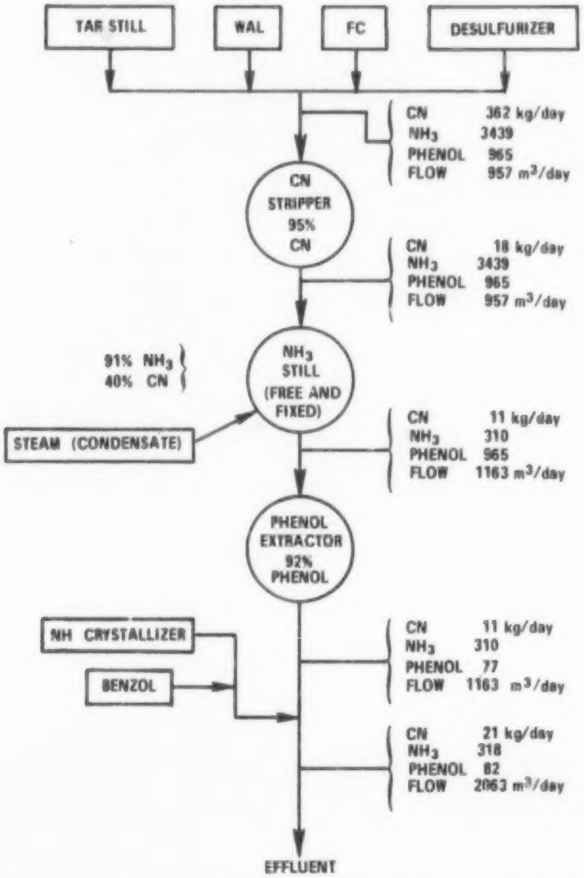

TAR STILL
WAL
FC
DESULFURIZER
CN 362 kg/day
NH_3 3439
PHENOL 965
FLOW 957 m^3/day
CN STRIPPER 95% CN
CN 18 kg/day
NH_3 3439
PHENOL 965
FLOW 957 m^3/day
91% NH_3
40% CN
NH_3 STILL (FREE AND FIXED)
STEAM (CONDENSATE)
CN 11 kg/day
NH_3 310
PHENOL 965
FLOW 1163 m^3/day
PHENOL EXTRACTOR 92% PHENOL
NH CRYSTALLIZER
BENZOL
CN 11 kg/day
NH_3 310
PHENOL 77
FLOW 1163 m^3/day
CN 21 kg/day
NH_3 318
PHENOL 82
FLOW 2063 m^3/day
EFFLUENT

Figure 4. Flow diagram for treatment level I for wastes from tight recycle.

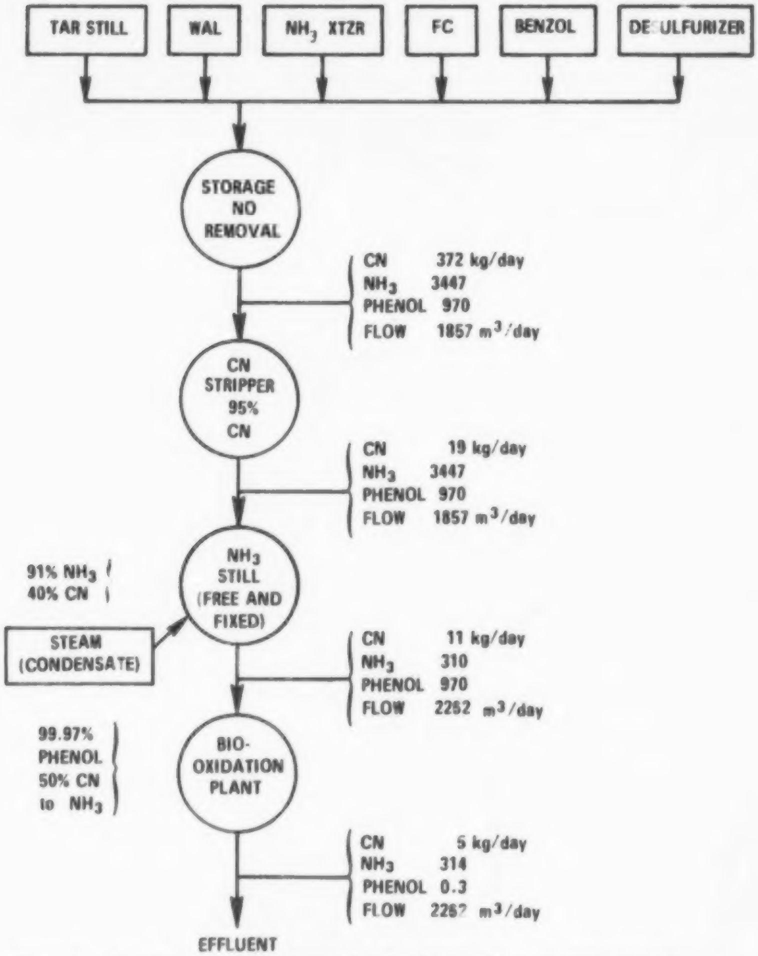

TAR STILL
WAL
NH$_3$ XTZR
FC
BENZOL
DESULFURIZER
STORAGE NO REMOVAL
CN 372 kg/day
NH$_3$ 3447
PHENOL 970
FLOW 1857 m^3/day
CN STRIPPER 95% CN
CN 19 kg/day
NH$_3$ 3447
PHENOL 970
FLOW 1857 m^3/day
91% NH$_3$
40% CN
NH$_3$ STILL (FREE AND FIXED)
STEAM (CONDENSATE)
CN 11 kg/day
NH$_3$ 310
PHENOL 970
FLOW 2262 m^3/day
99.97% PHENOL
50% CN to NH$_3$
BIO-OXIDATION PLANT
CN 5 kg/day
NH$_3$ 314
PHENOL 0.3
FLOW 2262 m^3/day
EFFLUENT

Figure 5. Flow diagram for treatment level II for wastes from tight recycle.

biological plant is similar to an existing facility at Bethlehem Steel and is designed to reduce the carbonaceous oxygen demand, with performance primarily set for phenolics reduction. These treatment systems do not precisely correspond to treatment levels designed to meet current EPA BPCTCA or BATEA limits. However, Level I meets BPCTCA guidelines for cyanide and ammonia; Level II meets BPCTCA guidelines and the BATEA guideline for phenol.

The eight different control strategies each result in pollutant emissions to the air, water, and land. Air emissions originate from the coke quench tower, from the open cooling towers, and from the power plant supplying electricity and/or steam to the treatment process units. Water emissions arise from coke plant wastewaters, from blast furnace wastewaters which account for pollutants transferred by wastewater quenching, and from power plant waste heat discharges. Land emissions originate at the power plant, the quench tower, the boiler water treatment plant, the coke plant ammonia still, and the coke plant biological treatment plant.

The foundation of the analysis is the construction of an inventory of all principal pollutants emitted to air, water, and land for each of the selected control strategies. Figure 6 shows the daily

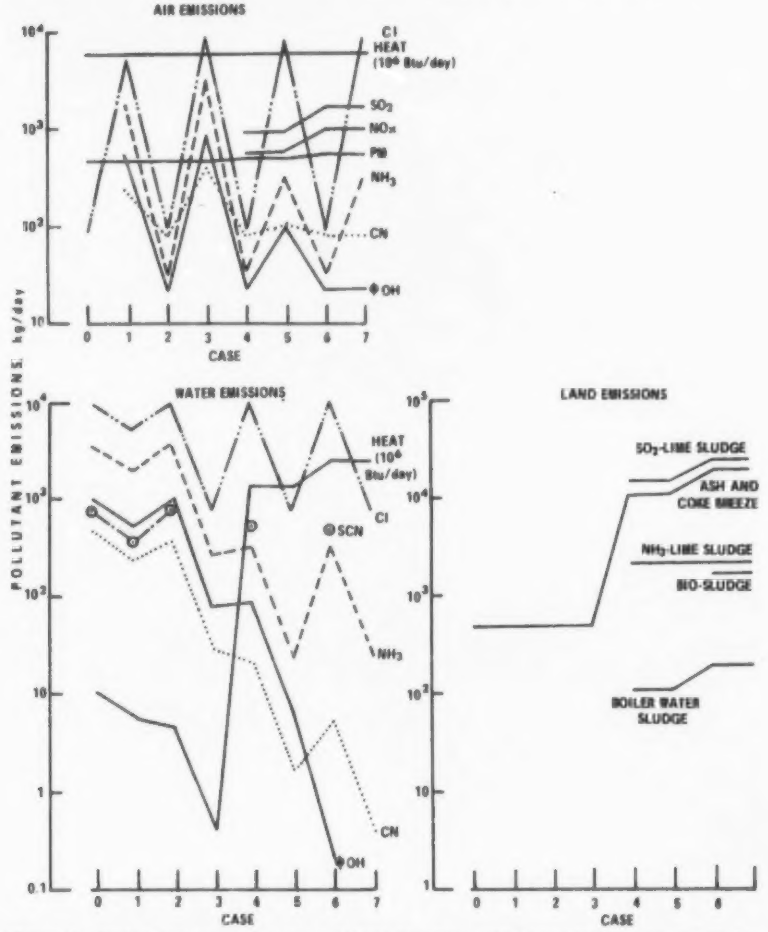


Figure 6. Emissions inventory for a 3,810 kkg/day (4200 ton/day) coke plant for light selected strategies.

emissions for a selected list of pollutants from each of the active operations for each control strategy. Measures were generated for eight pollutants emitted to the air, six pollutants to the water, and five pollutants to the land. By itself, this accounting of the residuals shows the relative complexity of the problem. It remains for the community and the regulatory agency to develop an aggregate summation of these different residuals in order to select an overall best strategy for the environment as a whole.

CROSS-MEDIA ANALYSIS

Comparing the complete inventory of emissions with the original wastewater loads (Figure 6, Case 0) shows that the reduction of emissions of ammonia, cyanide, and phenol to the water involves the generation and discharge of many other pollutants and treatment residuals to the air and land. A comparison of the relative environmental impact of the different strategies demands the ability to compare trade-off effects, i.e., the effect on the environment of reducing mass emissions of pollutants to the water while increasing mass discharges of other pollutants to the air and land. Reiquam, Dee, and Choi at the Battelle Memorial Institute under a contract sponsored by the Council on Environmental Quality and the EPA developed a technique for this purpose, termed Cross-Media Analysis.[5] This analysis starts with a mass emission inventory. A hierarchical arrangement of weights is developed consisting of two levels: media weights and pollutant weights. The first level of weights for air, water, and land may be regional or applicable to the country as a whole. The second level of pollutant weights establishes a mechanism for allocating relative fractions of each of the media weight totals to each pollutant. Choices between alternative strategies are based on the relative values of a numerical index calculated from the Cross-Media Analysis.

The environmental degradation index (EDI) is the arithmetic sum of the weighted damages for each pollutant in each media,

$$EDI = \Sigma p d_{p,s}$$

where p is the pollutant index and

$d_{p,s}$ is the damage function for a selected strategy, s, with $(0 \leq d_{p,s} \leq 1)$;

M_p is a modifier function which accounts for the dispersal and persistence of the pollutant $(0.1 \leq M_p \leq 0.8)$; and

W_p is the weight assigned to the pollutant, p, relative to the other pollutants $(pW_p = 1000)$.

A large value of the EDI means a large expectation of environmental degradation. Of course, the nature of the weighting scheme does not permit one to interpret the number absolutely. However, it is useful for comparing various control strategies. The algebraic difference between $(EDI)_o$ for a base case strategy and the $(EDI)_s$ for some other strategy is defined as the strategy effectiveness index $(SEI)_s$:

$$(SEI)_s = (EDI)_o - (EDI)_s$$

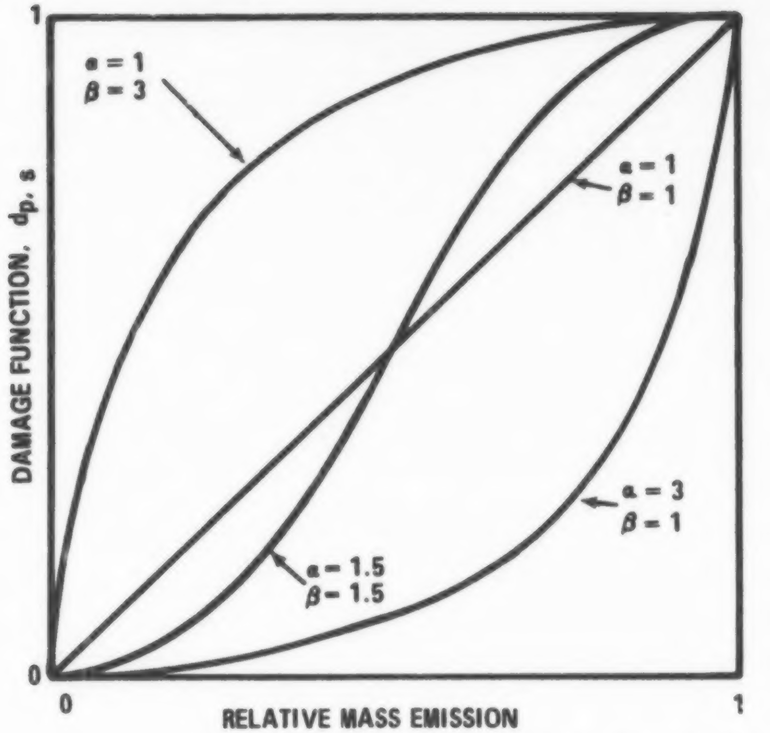
Values of SEI which are positive are interpreted as having a net improvement over the base case, whereas negative values of the SEI imply a net environmental degradation. This value of the SEI is the final basis for comparing, ranking, and choosing between control strategies.

This study used two sets of pollutant weights: one was based on choices made by steel industry experts at Battelle Institute (BMI); the second was selected by the authors (CMU) from a consideration of several sets of national air and water quality criteria.[6,7] Table 4 compares the relative weights. Both sets of choices assign approximately the same emphasis to each media, with air and water both ranked above the land. The CMU system distributes the pollutant weights less evenly than does BMI and focuses on phenol in water as being the most critical pollutant to control.

The mass emission inventory shown graphically in Figure 7

TABLE 4. POLLUTANT WEIGHTS (W_P) AND MODIFIER FUNCTION (M_P) FOR COKE PLANT WASTEWATER STUDY

	CMU weights			BMI weights		
Pollutant	W_p	M_p	W_pM_p	W_p	M_p	W_pM_p
To water:						
NH_3	5	0.6	3	52	0.6	31
Phenol	321	0.5	160	84	0.5	42
CN	22	0.5	11	74	0.5	37
Thiocyanate	3	0.5	2	56	0.5	28
Cl	1	0.6	1	33	0.6	20
Heat	22	0.5	11	74	0.5	37
Sum	374			373		
To land:						
Ash, coke breeze	41	0.5	20	42	0.5	21
SO_2-Lime sludge	54	0.6	32	58	0.6	35
NH_3-Lime sludge	54	0.6	32	58	0.6	35
Boiler water sludge	54	0.6	32	58	0.6	35
Biological sludge	54	0.6	32	58	0.6	35
Sum	255			274		
To air:						
NO_X	30	0.5	15	22	0.5	11
SO_2	70	0.7	49	43	0.7	30
PM	60	0.8	48	56	0.8	45
NH_3	26	0.5	13	47	0.5	24
Phenol	48	0.4	19	56	0.4	22
CN	82	0.4	33	60	0.4	24
Cl	25	0.4	10	47	0.4	19
Heat	30	0.5	15	22	0.5	11
Sum	371			353		
Total	1000			1000		



The damage function is assumed to be the cumulative Beta Function based on two parameters, α and β.

Mean of distribution is $[\alpha / (\alpha + \beta)]$ and the variance of the distribution is $[\alpha\beta / (\alpha + \beta)^2 (\alpha + \beta + 1)]$.

For all cases, the damage function is 1 where the relative emission is 1, that is, the actual emission is maximum.

When the actual emission is zero, the damage function is zero.

The following ranges of α and β were studied:

α \ β	1.0	2.0	3.0
1.0	X	X	X
2.0	X	X	X
3.0	X	X	X

Figure 7. The damage function.

must be converted to a set of numbers between 0 and 1, to be expressed as the damage function, d_p, for the Cross-Media Analysis. This study examined the sensitivity of the EDI to the procedure used for calculating damage. The simplest damage function imaginable scales damage as a linear function of the mass of pollutant discharged. One may choose damage functions to scale relative emissions nonlinearly, so as to place heavy damage on any small emission or to delay assignment of damage until a large fraction of the largest possible emission is reached (Figure 7). The results of the sensitivity of the relative rank of the coke plant strategies for nine damage functions are shown in Table 5 Using either the CMU or the BMI weighting functions and the various damage functions, the relative ranks of the coke plant wastewater strategies are nearly the same. By comparing absolute values of the SEI calculations as well as the sensitivity of the ranks for each strategy, it is possible to assemble the qualitative grouping of the coke plant strategies shown in Table 6.

TABLE 5. FREQUENCY DISTRIBUTION OF ALTERNATIVE STRATEGIES BY RANK FOR NINE DAMAGE FUNCTION CHOICES

Case	Tank								Average
	1	2	3	4	5	6	7	8	rank
Number of times case ranked as shown (CMU weights)									
0	X	1	X	2	2	3	1	X	5.00
1	1	1	X	4	1	1	1	X	4.11
2	X	X	X	1	5	3	X	X	5.22
3	6	1	X	2	X	X	X	X	1.78
4	2	4	2	X	1	X	X	X	2.33
5	X	2	7	X	X	X	X	X	2.78
6	X	X	X	X	X	2	7	X	6.78
7	X	X	X	X	X	X	X	9	8.00
Number of times case ranked as shown (BMI weights)									
0	X	2	1	X	1	5	X	X	4.67
1	3	2	1	X	3	X	X	X	2.79
2	X	X	2	2	5	X	X	X	4.33
3	6	2	X	1	X	X	X	X	1.56
4	X	X	1	4	X	4	X	X	4.78
5	X	3	4	2	X	X	X	X	2.89
6	X	X	X	X	X	X	X	9	8.00
7	X	X	X	X	X	X	9	X	7.00

COMPARISON OF WASTEWATER CONTROL STRATEGIES

Table 7 shows that control of coke plant wastewaters does result in environmental improvement for the watercourse to which the

TABLE 6. GROUPING OF WASTEWATER TREATMENT STRATEGIES

Case	Treatment	Qualitative ranking
3	Raw wastewater effluent; tight recycle; wastewater quench	Preferred
5	Level I treatment; tight recycle; wastewater quench	Preferred
1	Raw wastewater effluent; loose recycle; wastewater quench	Better than base case
4	Level I treatment; tight recycle; wastewater discharge to watercourse	
2	Raw wastewater effluent; tight recycle; wastewater discharge to watercourse	Base case
0	Raw wastewater effluent; loose recycle; wastewater discharge to watercourse	
6	Level II treatment; tight recycle; wastewater discharge to watercourse	Not preferred
7	Level II treatment; tight recycle; wastewater quench	

TABLE 7. NET ENVIRONMENTAL IMPACT FOR TWO SELECTED SETS OF POLLUTANT WEIGHTS AND A S-SHAPED DAMAGE FUNCTION

$(\alpha = \beta = 1.5)$

Case	Air	Water	Land	Total	Rank
		Strategy effectiveness index (CMU weights)			
0	0	0	0	0	5
1	−39	85	0	46	4
2	− 5	3	0	− 2	6
3	−75	172	0	97	1
4	−16	162	− 70	76	2
5	−30	170	− 70	70	3
6	−28	164	−148	−12	7
7	−39	166	−148	−21	8
		Strategy effectiveness index (BMI weights)			
0	0	0	0	0	5
1	−47	77	0	30	2
2	− 3	5	0	2	6
3	−89	154	0	65	1
4	−12	92	− 76	4	4
5	−34	136	− 76	26	3
6	−20	82	−161	−99	8
7	−40	120	−161	−81	7

plant discharges its wastes. Control strategy Case 0 (loose recycle, no wastewater treatment, discharge to the river) is chosen as the base case against which all other strategies are compared. The least desirable control strategies have negative SEI values, indicating a net environmental damage when compared with that of the base case. In contrast, a large positive total SEI value for a control strategy indicates net environmental improvement when compared with that of the base case. For all control strategies, and either weighting method, positive SEI values occur for the water media, indicating environmental improvement over the base case.

Note, however, that environmental improvement for the watercourse is coupled in every situation with degradation of the air and land media. Values of zero for the SEI mean that these cases are identical to the base case. Furthermore, in some cases the net environmental degradation of the air and land media are large enough to negate the improvement which has taken place in the watercourse. Environmental improvement in one media–here, water–is inextricably associated with deleterious cross-media effects, which may be large enough themselves to provide no net environmental improvement for the control effort.

CONCLUSIONS

The principal findings of this study apply to the coke plant problem in particular, but they suggest there may be grave consequences whenever there is stringent effluent regulation for separate media. Wastewater treatment provides environmental improvement for one media, water, but will lead to the degradation of the other media, air and land. This is the phenomenon of cross-media impact; energy requirements for treatment processes create new pollutant residuals which are smeared across all media. For some wastewater treatment practices, the *net* environmental improvement due to the practice is *negative*, i.e., cross-media effects are so large as to negate the beneficial effects of improving the water media. The frequency for which net degradation of the environment is forecast from this analysis depends on input parameter values and assumptions; this frequency rises sharply with the stringency of wastewater treatment.

It is useful to characterize the coke plant problem in three ways: by type of quench water, by level of process water recycle, and by level of treatment selected for wastewaters. The cross-media analysis leads to the following observations:

1. Quenching with coke plant effluents, regardless of their level of treatment, appears to be a preferred practice for the greatest net improvement of the environment. This practice is preferred to that of discharging effluent (at the same level of treatment) to watercourse.

2. Tight recycle of cooling waters rather than loose recycle ap-

pears to be preferred for the greatest net environmental improvement.

3. For the wastewater control case in which tight recycle of cooling waters is employed and the final effluent is used for wastewater quenching, *no* wastewater treatment is a preferred practice over either Level I or Level II treatment, if the greatest net environmental improvement is to be achieved.

4. For the wastewater control case in which tight recycle of cooling waters is employed and the final effluent is discharged to a watercourse, Level I is the preferred wastewater treatment if the greatest net environmental improvement is to be realized. For this case, this treatment level is preferred over the alternatives of no treatment or Level II treatment.

5. These results suggest that the current EPA effluent standards for by-product coke plants, particularly the BATEA (1983) limits, are too stringent to maximize the net environmental improvement which can result from the treatment and disposal of coke plant wastewaters.

The results of this study clearly support the contention that levels of environmental control must be considered very carefully if maximum improvement of the environment is to take place; stringent control of emissions is not necessarily the best course of action. However, this analysis, like all analyses, is an approximation of reality, and not reality itself. In particular, the cross-media technique requires many assumptions which are open to question and interpretation. Nevertheless, the results of the study appear robust enough that strong conclusions can be stated regarding current by-product coke plant effluent limitations. This analysis is offered not to exacerbate the current controversy regarding treatment and disposal of coke plant wastewaters, but to move the controversy toward more rational emphasis on net improvement of the environment, rather than emphasis on single media regulations and solutions.

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TANNERY WASTE MANAGEMENT

J. David Eye

ABSTRACT

Tanning of hides into leather creates large volumes of highly polluted wastes. Initially most of the pollutants are contained in relatively small-volume, highly concentrated waste fractions. Separation and pretreatment of waste fractions before blending for clarification and biological treatment appears to be the most efficient method for managing these wastes.

Plant arrangement and discharge schedules often prevent effective separation of the waste fractions, hence it may be necessary to treat the combined wastes as a single effluent. When separation and pretreatment are possible, the usual procedure is to oxidize the sulfides with air using manganese as a catalyst and to precipitate chrome as chromium hydroxide. In some cases, flue gas is used to lower the pH of the lime-bearing wastes.

The treatment of the combined waste streams usually includes: screening, primary clarification with or without coagulants, aerobic biological treatment by activated sludge or aerated lagoons or a combination of aerated and nonaerated lagoons, final clarification, and disinfection if required. Treatment efficiencies for BOD and suspended solids removal often are well above 90%.

The author has specialized in the in-plant removal of sulfides and chrome and in the use of aerobic-anaerobic lagoon systems for final treatment. Design criteria and operating data from some of the projects that he has designed and constructed are presented. Operational problems, particularly those related to cold weather operation, are discussed.

INTRODUCTION

The tanning industry has long been recognized as a major contributor to water pollution because of the highly pollutional nature of the constituents of untreated tannery effluents. The total volume of tannery wastes discharged in the United States, however, amounts to only about 16 × 10^9 gal (6.056 × 10^7 m^3) per year, a rather small volume when compared with the discharges from many other wet industries.

There are two basic types of tanning in use in some 300 tanneries in the United States today—vegetable tanning and chrome tanning or some combination thereof. Chrome tanning, used mainly for producing side leather, accounts for 85% to 90% of the total production, and vegetable tanning, which is used for heavy leathers, accounts for only about 10% to 15% of the total. Domestic cattle hides make up the bulk of raw materials used, with some 18 to 20 million being tanned annually. Sheep skins and pig skins are also tanned but constitute only a small percentage of the total weight of hide substance tanned.

The tanning of animal skins is accomplished by chemically and mechanically removing all of the extraneous hide substance from the collagen fibers, which then combine with chrome salts and/or vegetable extracts to produce leather. The materials used in tanning operations include water, sulfides, lime, ammonium sulfate, sulfuric acid, chromium sulfate, vegetable extracts, sodium carbonate, detergents, natural and synthetic oils, dyes, filling agents such as starch and clay, solvents, and a variety of organic finishes. The tannery effluents therefore can be expected to contain various amounts of all of the materials used in tanning plus the unwanted hide substance extracted during tanning.

TANNING OPERATIONS

A large fraction of the hides that are tanned are received at the tannery in salt- or brine-cured form. Only a small percentage of the total number of hides tanned are processed from the fresh state.

The major tanning operations include: washing and soaking to remove extraneous blood, manure, salt, and dirt and to restore moisture to brine-cured hides; hair removal with caustic (usually lime) and sulfides (this step may only loosen the hair for mechanical removal or it may be severe enough to completely dissolve the hair); bating with enzymes and ammonium salts to remove excess caustic and prepare the hides for tanning; fleshing to remove excess fat and muscle tissue from the animal side of the hide (this may be done before hair removal or afterward); splitting of the hide into two or more layers (this may be done after hair removal or after tanning); pickling or treating the bated hides with salt and sulfuric acid; tanning with either vegetable extracts or chromium salts; drying; shaving to achieve the desired thickness (weight); buffing or sanding to smooth the surface; fat liquoring to restore oils; coloring; and finishing.

The sequence of operations varies in individual tanneries depending on the end product desired. Also, some operations used for producing side leather are not required for heavy vegetable-tanned leathers. The usual tanning steps are illustrated in Figure 1.

CHARACTERISTICS OF TANNERY WASTES

In cattle hide tanneries, the volume of wastes generated range

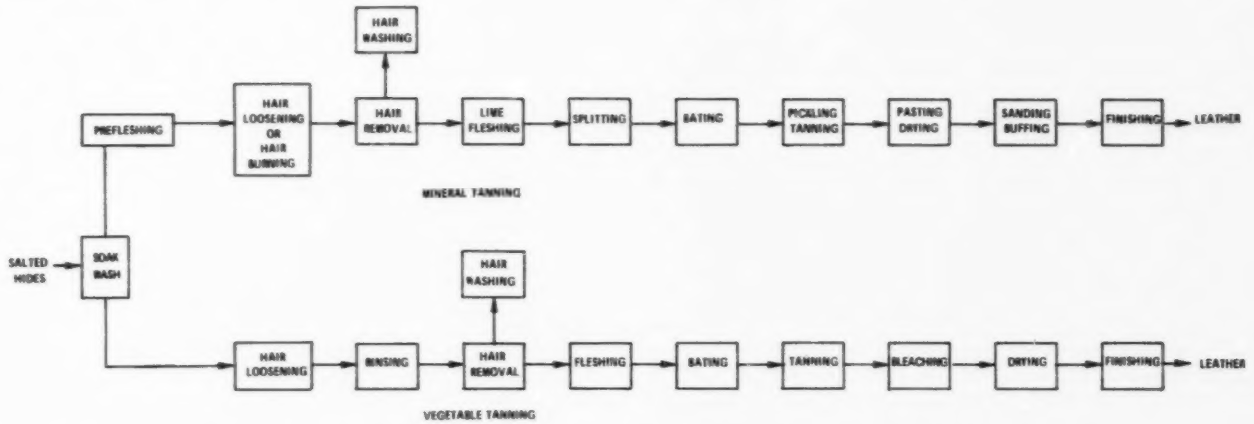
HAIR WASHING
PREFLESHING
HAIR LOOSENING OR HAIR BURNING
HAIR REMOVAL
LIME FLESHING
SPLITTING
BATING
PICKLING TANNING
PASTING DRYING
SANDING BUFFING
FINISHING
LEATHER
MINERAL TANNING
SALTED HIDES
SOAK WASH
HAIR WASHING
HAIR LOOSENING
RINSING
HAIR REMOVAL
FLESHING
BATING
TANNING
BLEACHING
DRYING
FINISHING
LEATHER
VEGETABLE TANNING

Figure 1. Typical flow diagram for tanning.

from 100 to 1000 gal (0.3785 to 3.785 m^3) per hide processed. Since most tanning operations are of the batch type, the waste flow is highly variable both in volume and in constituents during an operating day. The fluctuations observed for one tannery effluent are illustrated in Figure 2.

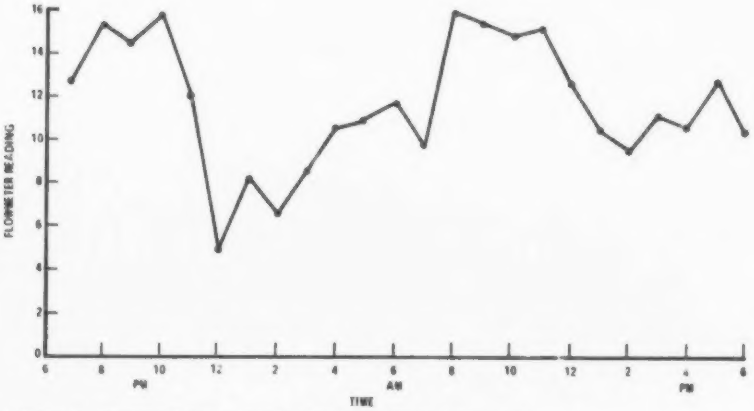

Figure 2. Fluctuations in waste discharge from a tannery.

Detailed studies of tannery wastes by the author have revealed that a large fraction of the pollutants of concern initially are contained in relatively small-volume waste fractions. The large-volume waste fractions normally are derived from rinsing operations, and as such they contain relatively low concentrations of pollutants. In fact, it has been found that 75% to 80% of the BOD and suspended solids are derived from waste streams that constitute only about 30% to 40% of the total tannery effluent volume. Values listed in Table 1 for the wastes from a vegetable tannery unhairing

TABLE 1. CHARACTERISTICS OF BEAMHOUSE WASTE FRACTIONS

Waste fraction	Flow, gpd*	COD, mg/l	Suspended solids, mg/l	pH
Wash water	25,000	2,100	1,300	6.8
Soak water	10,000	2,200	1,000	7.8
Lime water	10,000	11,900	30,300	12.3
Rinse water	20,000	2,500	4,900	12.3
Hair water	15,000	2,500	3,100	12.3
Fleshing water	5,000	3,600	3,100	12.3
Bate water	55,000	1,700	1,000	9.0

* Note: 1,000 gpd = 3.785 m^3/day.

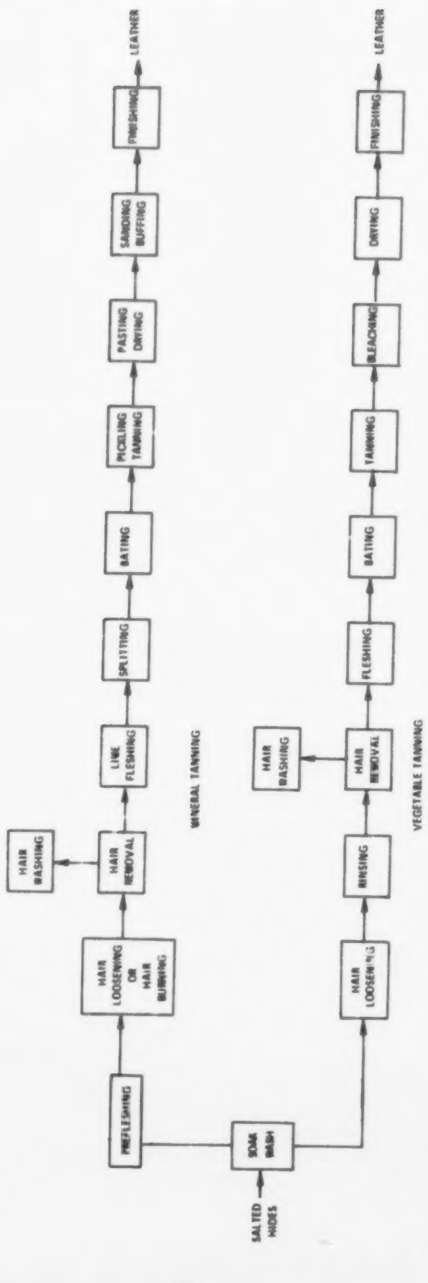
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Figure 1. Typical flow diagram for tanning.

system illustrate the wide variability in individual waste stream characteristics.

Typical waste constituents and concentrations for the mixed wastes from a side leather tannery are listed in Table 2.

TABLE 2. TYPICAL WASTE CHARACTERISTICS

Waste parameter	Concentration range, mg/l
pH	9.0- 12.0
BOD	2,000-3,000
COD	2,500-4,000
TSS	2,000-3,000
TS	4,000-9,000
Cl	2,500-4,000
TKN	150- 250
NH_3	80- 125
$S^=$	100- 250
Cr^{+3}	100- 250
Oil and grease	100- 250

WASTE MANAGEMENT PROCEDURES

An efficient plan for the management of tannery wastes must begin at the points of waste generation — the individual tanning operations. Careful control of the amounts of water and processing chemicals used can effectively reduce the cost and difficulty of treating the residual waterborne pollutants. Likewise, changes in processing equipment can be highly beneficial in reducing the amount of water and chemicals used. For example, during the past 5 years many tanners have substituted mechanical hide processors for the traditional paddle vats and drums for unhairing and tanning operations. This step alone can reduce water consumption by as much as 50% and at the same time effect significant reductions in the amount of chemicals used because of better contact between the hides and the tanning solutions. The hide processors also facilitate the separation of the waste fractions for pretreatment and/or recovery.

Pretreatment of individual waste streams generally is applied to the unhairing wastes and the spent chrome tan liquors. Since the unhairing wastes initially contain most of the sulfides found in tannery effluents, consideration should be given to oxidizing the sulfides to a more stable form before these wastes are mixed with other waste fractions. It has been found that the sulfides can be eliminated completely by air oxidation with manganese as a catalyst in 3 to 6 hr. The concentration of manganese used is usually 5% to 10% of the sulfide concentration. For example, if the sulfide concentration is 5,000 mg/l as $S^=$, the manganese concentration would be 250 to 500 mg/l as MN^{++}.

The efficiency of air oxidation can also be exemplified in terms of the oxygen transfer rates. In most biological oxidation systems, an oxygen transfer rate of 2 to 4 lb/hr/hp (1.4×10^{-3} to 2.8×10^{-3} kg/kg-cal) is observed. In a manganese-catalyzed sulfide reaction, the oxygen transfer rate usually ranges from 25 to 65 lb/h/hp 1.8×10^{-2} to 4.6×10^{-2} kg/kg-cal). The portion of the total BOD contributed by the sulfides therefore can be removed more efficiently by air oxidation with manganese as a catalyst than through biological oxidation.

It should be mentioned that the unhairing wastes can be screened, refortified, and reused directly, or the sulfides can be expelled as H_2S and redissolved in a sodium hydroxide solution for reuse. These two recovery methods are being used to a limited extent at present. Considerable attention also is being given to the extraction of the proteins from the unhairing wastes.

In most side leather tanneries only about 65% to 75% of the chrome used actually remains in the leather. The remainder of the chrome is discharged in the tannery wastes. While there is no conclusive evidence that the chromium in the effluent interferes with waste treatment processes, it does pose a problem in the disposal of residual sludges derived from treatment processes.

By separating the spent tan liquors and raising the pH to 9.5 to 11.5, the chrome can be effectively precipitated in the hydroxide form. Once precipitated, it can be redissolved and reused in preparing fresh tanning solutions. In some tanneries, the spent chrome liquor is collected, refortified and reused directly for tanning.

Irrespective of the separation, pretreatment and/or reuse practices used, all of the tannery wastes must be screened before further treatment. Several types of screens are in use, and all have certain limitations and/or operational problems. The most frequent problem encountered is that of clogging with grease and chemical deposits, and frequent or continuous cleaning usually is required.

Following screening, the wastes can be clarified to remove the settleable solids. The use of inorganic coagulants and organic polyelectrolytes enhances the settling process and ultimately improves the dewatering characteristics of the sludge. In general, clarification can be expected to remove 50% to 60% of the BOD and as much as 90% of the suspended solids. The settling characteristics and the effectiveness of clarification on the unhairing wastes from a vegetable tannery are illustrated in Figures 3 and 4.

The sludge derived from clarification is large in volume, has a high moisture content (90% to 95%), and is often difficult to dewater. Pressure filters, vacuum filters, centrifuges and sand drying beds are commonly used to dewater the sludge to a moisture content of 55% to 80%. Dewatered tannery sludges normally are placed in landfill, although considerable interest is being shown in agricultural applications. The dewatering characteristics on a sand bed of the sludge derived from clarification of the unhairing wastes from a vegetable tannery are indicated in Table 3.

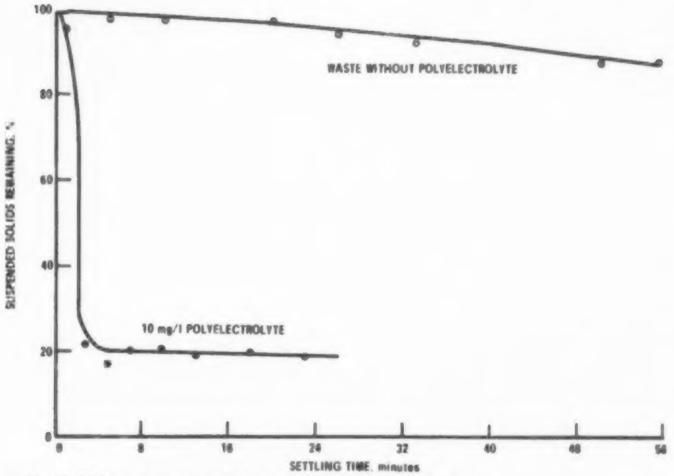

Figure 3. Settling characteristics of lime-bearing wastes.

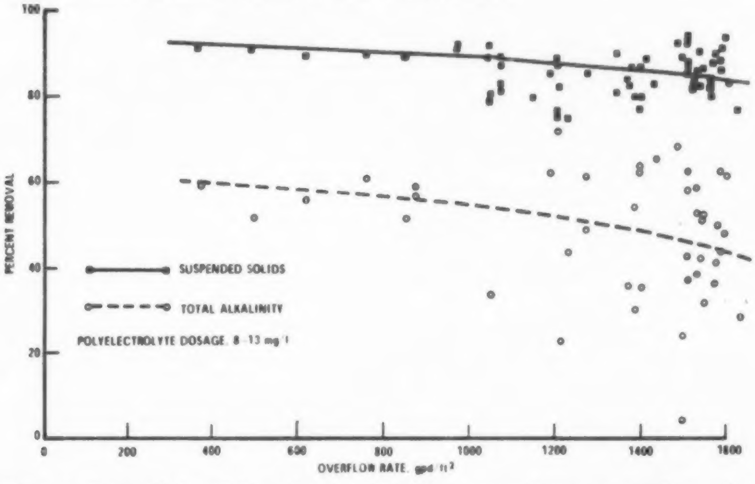

Figure 4. Suspended solids and total alkalinity removal versus overflow rate. Note: 1 gpd/ft^2 = 4.1 x 10^{-2} m^3/day per m^2.

TABLE 3. SLUDGE DRYING CHARACTERISTICS*

Time, days	Depth of sludge on bed, in.				Weather	
	No. 1	No. 2	No. 3	No. 4	Type	Temperature
0	2	4	6	8	Clear	25 F (−4 C)
1	¼	½	1¼	2	Cloudy	28 F (−2 C)
2	¼	½	1¼	2	Snow	22 F (−6 C)

* Sludge derived from unhairing wastes treated with 5 to 10 mg/l of anionic polyelectrolyte. Note: 1 in. = 2.54 cm.

The clarified tannery wastes are amenable to aerobic and anaerobic biological treatment. Activated sludge systems, oxidation ditches, and aerated lagoons are being used successfully to oxidize the organic matter in tannery effluents. Tannery wastes normally have a high organic nitrogen content and a relatively low concentration of phosphorous. Adjustment of the nutrient balance therefore may be required for optimum biological oxidation. A detention time of 12 to 24 hr and a sludge age of about 5 days appear to be necessary for activated sludge.

Effluent BOD values as low as 10 to 20 mg/l can be achieved routinely with any of the aerobic biological systems during warm weather, provided the final clarifier is properly designed and operated. When the waste temperature drops below about 15 C, treatment efficiency is usually reduced, particularly in aerated lagoons where the ratio of BOD to active biomass is high. Activated sludge units and oxidation ditches are not as sensitive to low temperatures as are the aerated lagoons because it is possible to maintain a lower BOD to biomass ratio.

The author has specialized in the use of aerobic-anaerobic lagoon systems for treating tannery wastes. In some of the systems, extensive separation and pretreatment of waste streams are carried out before biological oxidation; in others, the total wastes are only screened and clarified before being admitted to the lagoon system. The lagoon systems normally utilized consist of stratified aerobic-anaerobic units in series with anaerobic lagoons, or aerobic units in series with anaerobic lagoons.

One such system designed for a tannery in New England is illustrated in Figure 5. The wastes are screened then allowed to flow through a large lagoon where the settleable solids are removed

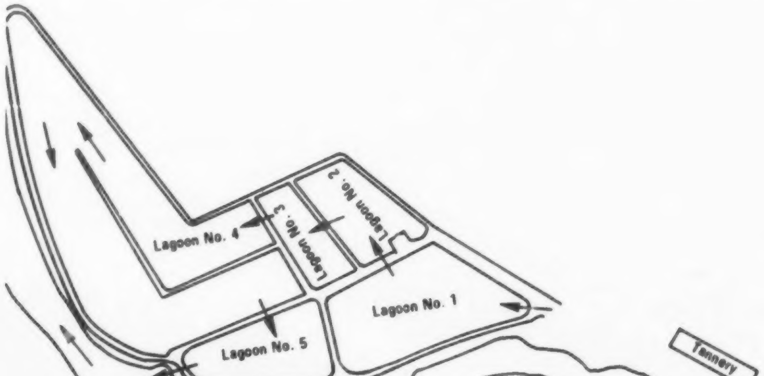

Figure 5. Lagoon system designed for a New England tannery.

by settling. The pH of the sludge lagoon is maintained above 11.0 at all times to eliminate odors. The accumulated sludge is not removed, hence this lagoon will ultimately have to be abandoned. Initial calculations indicated that the sludge lagoon would have a useful life of 15 years, but recent surveys indicate it will be useful for at least 20 years.

The design criteria for the system are listed in Table 4.

The expected performance of the system in terms of effluent BOD values is outlined in Table 5.

TABLE 4. DESIGN CRITERIA FOR A 0.60-MGD TANNERY*

Constituent	mg/l	lb/day
BOD — 5 day, 20°C screened waste	1,500	7,500
BOD — 5 day, 20°C settled waste	1,000	5,000
Suspended solids	1,900	9,500
Suspended solids after settling	500	2,500
COD	3,000	15,000
NH_3 nitrogen	50	250
Organic nitrogen	90	450

* Note: 1 lb = 0.453 kg.

TABLE 5. EXPECTED PERFORMANCE OF SYSTEM

Item	Amount
BOD of total waste	1,850 mgl
BOD of clarified waste	1,000 mgl
BOD of final effluent (summer)	100 mgl
BOD of final effluent (winter)	250 mgl
BOD to receiving stream (summer)	500 lb/day
BOD to receiving stream (winter)	1,250 lb/day

Lagoon Numbers 2, 3, 4, and 5 provided detention times of 3, 3, 30, and 2 days, respectively, at the design rate of flow. Initially it was assumed that Lagoon Numbers 2, 3, and 4 would be operated as stratified aerobic-anaerobic units and Number 5 as an anaerobic lagoon. It was necessary therefore to estimate the distribution of the BOD among the lagoons so that adequate aeration capacity could be provided.

Since the tannery operated only 5 days each week, there was little flow on 2 days. The BOD derived from each operating day would therefore affect each lagoon differently. Laboratory studies showed that the ultimate BOD was exerted in about 20 days; hence, the BOD for each day for a 20-day period was routed through the lagoons by assuming that plug flow pertained. The routing procedure is illustrated in Figure 6.

DAY	LAGOON	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W
MON	No. 2	1	2	3	4/2																				
	No. 3				4/2	5	6	7	8	9/2															
	No. 4									9/2	10	11	12	13	14	15	16	17	18	19	20				
TUES	No. 2		1	2	3	4/2																			
	No. 3					4/2	5	6	7	8	9/2														
	No. 4										9/2	10	11	12	13	14	15	16	17	18	19	20			
WED	No. 2			1	2	3	4	5	6/2																
	No. 3								6/2	7	8	9/2													
	No. 4											9/2	10	11	12	13	14	15	16	17	18	19	20		
THURS	No. 2				1	2	3	4	5	6/2															
	No. 3									6/2	7	8	9/2												
	No. 4												9/2	10	11	12	13	14	15	16	17	18	19	20	
FRI	No. 2					1	2	3	4	5	6/2														
	No. 3										6/2	7	8	9	10	11/2									
	No. 4															11/2	12	13	14	15	16	17	18	19	20

Figure 6. Exertion of BOD in lagoons 2, 3, and 4. Note: The numerical values represent the progression of the BOD to the lagoons from 0 to 20 days for a 5-day plant operating schedule.

The BOD loadings calculated for Lagoon Numbers 2, 3, and 4 are listed in Table 6.

TABLE 6. BOD EXERTED IN LB/DAY/LAGOON*

Day	Lagoon No. 2	Lagoon No. 3	Lagoon No. 4
Monday	3,700	950	850
Tuesday	4,050	975	915
Wednesday	4,200	975	1,000
Thursday	4,225	1,050	1,065
Friday	4,275	1,150	1,135
Saturday	2,050	1,100	1,330
Sunday	1,600	975	1,130
Total	24,100	7,175	7,425

* Note: 1 lb = 0.453 kg.

Floating aerators were selected for this installation. It was assumed that the oxygen transfer capability of the aerators to tannery wastes would be 2 lb/hr/hp (1.4×10^{-3} kg/kg-cal). On this basis, 90, 25, and 28 hp were required for Lagoon Numbers 2, 3, and 4, respectively (1 hp $= 1.068 \times 10^{-1}$ kg-cal/min).

When the system was placed in operation, Lagoon Numbers 2, 3, and 5 were aerated, and Number 4 was allowed to function as a facultative lagoon. The results obtained during 21 months of operation are presented in Table 7.

The accumulated data show that the system gave a higher degree of treatment than was expected during the warm months of the year. When the temperature of the wastes fell below 10 C, treatment efficiency declined significantly with some observed values exceeding design expectations. Part of the reduction in treatment efficiency can be attributed to the poorer settling experienced when the viscosity of the wastes increased with decreasing temperature. Since no provision was made for sludge recycling this reduction in treatment efficiency could not be counteracted because no increased biomass concentration in the aerated lagoons could be effected.

The reduction in the total Kjeldahl nitrogen (TKN) is of interest, particularly with respect to the organic nitrogen fraction of the TKN. Even during the winter months, most of the organic nitrogen was removed either through precipitation or denitrification. The nitrate concentration in the effluent never was observed above a few mg/l. The chromium content likewise remained at low levels for the entire period.

The major operational problems encountered have been those caused by extremely low air temperatures. If an aerator stops running for more than a few minutes, the wastes will freeze and the aerator usually cannot be restarted until the ice thaws in late spring. A major power failure during the winter months therefore could completely eliminate the aerated phases of this system. For-

TABLE 7. FINAL EFFLUENT CHARACTERISTCS
(mg/l)

Sample date	BOD	TS	TKN	NH_3	Cr	Grease
5/17/73	76	108	45	18	3.5	26
6/22/73	18	35	48	37	1.0	21
7/17/73	11	14	43	35	0.8	9
8/1/73	11	8	28	26	0.5	9
8/15/73	10	13	27	25	0.7	16
9/5/73	15	25	35	30	0.8	8
9/19/73	14	16	34	31	0.6	57
10/3/73	18	6	33	30	0.4	26
10/25/73	20	20	47	36	0.7	19
11/2/73	18	34	54	43	0.9	73
11/28/73	38	55	56	42	1.3	72
12/12/73	61	61	57	39	3.7	72
12/26/73	118	10	47	27	1.7	28
1/14/74	168	10	56	29	0.7	5
1/28/74	241	7	97	35	1.1	13
2/13/74	258	12	48	43	3.0	10
2/28/74	361	68	62	36	5.4	289
3/14/74	324	96	33	27	4.2	21
3/28/74	333	166	44	35	4.6	36
4/17/74	238	85	36	32	2.0	49
4/30/74	146	524	34	27	4.0	—
5/15/74	110	181	40	33	3.5	96
6/6/74	56	71	45	39	1.8	42
6/27/74	16	95	50	47	1.0	54
7/16/74	28	24	42	40	1.0	29
7/30/74	14	268	35	34	0.8	10
8/19/74	12	63	36	34	0.2	30
8/29/74	19	4	44	42	0.5	130
9/17/74	16	18	54	52	0.8	30
10/1/74	13	27	55	53	0.9	70
10/15/74	18	122	54	52	0.5	120
10/31/74	35	308	54	51	0.8	230
11/15/74	12	48	54	50	1.0	70
11/21/74	46	249	53	49	1.8	180
12/17/74	76	73	48	42	2.0	60
12/31/74	176	125	50	43	2.0	30
1/15/75	222	774	42	34	2.0	30

tunately this has not happened in the 3 years that this system has been operating.

It must be emphasized that the system design was based on water quality standards in existence in 1971. The system will not meet current EPA effluent guidelines during the winter months, and extensive revisions will be effected during 1976.

DEVELOPING TREATMENT FOR TEXTILE WASTES

Jan Suschka

ABSTRACT

A variety of methods can be used for treating combined municipal and textile wastewater. Results presented here show that chemical treatment, although effective for pollutant and especially for color removal, requires large amounts of chemicals. The use of lime without any additional chemicals can be recommended. Complete color removal does not normally take place by coagulation and must be achieved by activated carbon adsorption.

Another approach using two-stage biological treatment was also shown to be effective. Good removal of organic pollutants and color can be obtained when an anaerobic fixed-bed filter followed by an activated sludge process is applied. But, as in the case of chemical treatment, total removal of color requires the additional step of activated carbon adsorption.

Development of the textile industry has included the use of many new methods and agents for fiber dyeing. The present list contains 3500 dyes—more than 2000 of them azoic dyes. Treatment of textile dye house effluent has therefore been a long and difficult problem.

The open literature contains many studies concerning the problem of treating textile wastewater by physical, chemical, and biological methods. The suitability of a method depends very much on the type and concentration of constituents in treated wastewaters. At present, no universal procedure can be recommended; but results of research can point to possible solutions and help with specific problems.

BIOLOGICAL TREATMENT OF TEXTILE WASTEWATERS

Activated sludge treatment of combined municipal and textile wastewater was reported by many authors to be an effective method, but the problem of color removal is controversial. Color removal rates with this method range from 0% to 99% because of the variety of dyes used by the textile industry and their varying resistance to biological degradation.

To investigate the suitability of various color removal methods, sewage was mixed with a prepared solution of dyes, detergents, and aids. The basic test mixture used for the first runs (Series I) is given in Table 1. Subsequent test runs (Series II) were carried out with a 0.1% dye bath/wastewater mixture (Table 2).

TABLE 1. COMPOSITION OF WASTEWATER USED IN TESTING THE ACTIVATED SLUDGE METHOD, SERIES I

Components added to settled municipal sludge	Concentration, mg/l
Reactive dye — lunasol red 5B	50
Basic dye — aniline red BLN	50
Sulphur dye — sulphur brown	50
Welan dye — Welan brown	50
Dispersant NNO	50
Fixative WOM	50
Total	300

TABLE 2. COMPOSITION OF THE 0.1% DYE BATH/WASTEWATER MIXTURE, SERIES II

Components added to settled municipal sewage	Components concentration, mg/l
Dyes:	
Aniline red BLN	4.17
Lunasol red 5B	5.00
Sulphur brown	3.34
Welan brown	6.67
Total	19.18
Assistants:	
Dispersant NNO	2.00
Elanofor	0.33
Lodegal MK	1.67
Rokaphenol N 8	0.66
Suphurol N2	0.08
Fixative WOM	6.67
Total	11.41
Acetic acid	10.0
Sodium sulphide	8.35
Sodium carbonate	8.35
Sodium sulphate	8.00

Laboratory-scale investigations were carried out in 5.71-liter aeration tanks aerated with surface rotors. The average BOD of the investigated mixture was 145 and 210 mg/l, respectively, in Series I and II. With a mixed volatile suspended solids content in the aeration tank on the order of 1 to 2 g/l and a detention time of 4.5 to 6.1 hr, the load of BOD was in the range of 0.20 to 0.95

g BOD/g MLVSS/day. The respective load of COD determined from filtered samples ranged from 0.25 to 1.35 g/g/day.

The removal efficiency of BOD and COD was given in Figure 1. By presenting the results of BOD removal as a relationship of the rate of removal (W) and the activated sludge load (L) (Figure 2), a mathematical expression can be given:

$$W = 2\frac{L}{2.2 + L}$$

where: W = BOD removal rate, d^{-1}
L = activated sludge load, g/g per day

With a relatively high BOD removal rate of 60% to 90% (Figure 1), no color removal (or ocassionally only a 20% rate) was obtained.

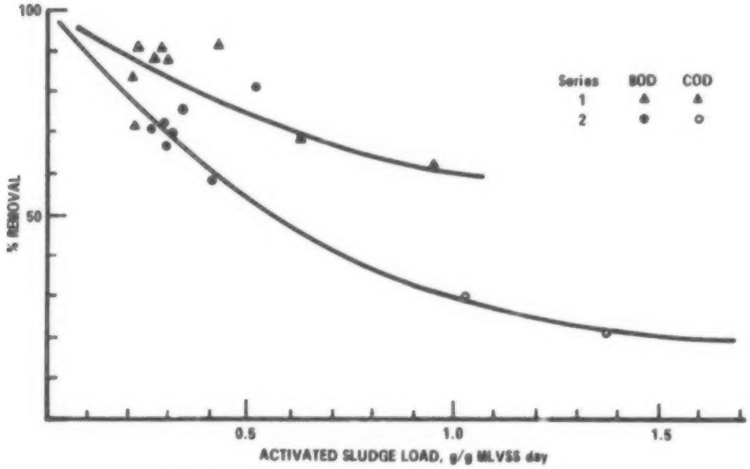

Figure 1. Relationship between BOD and COD removal and sludge loading.

On the basis of batch tests for each individual dye in admixture to sewage, it was shown that all four tested dyes were similarly resistant to biodegradation. A maximum removal rate of 5% was achieved for the reactive dye, lunasol red 5B. The dye Welan brown was removed to a similar degree. Higher color removal up to 10% was obtained for the sulphur dye (sulphur-brown). The highest removal rate, from 10% to 20%, was obtained for the basic dye, aniline red BLN.

All of the dyes as well as the dispersant NNO and fixative WOM were tested in an admixture with sewage, using a concentration of 300 mg/l. With such high concentrations of these compounds, very good BOD removal rates (50% to 86%) were achieved. Thus any

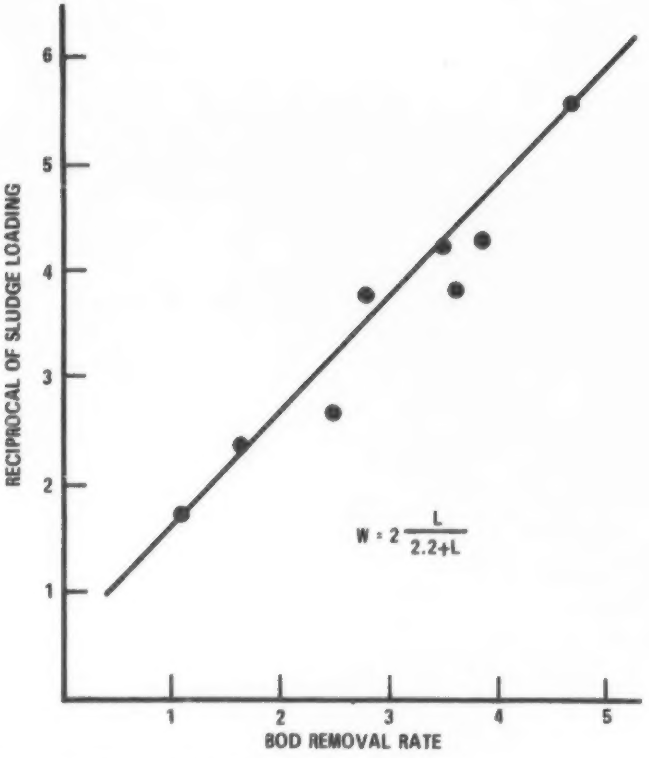

Figure 2. Efficiency of the activated sludge process.

toxic effect of these compounds could be noted. However, COD removal was only 20% to 35% for all compounds except the dispersant NNO, for which a 10% COD removal was obtained.

Distinct improvement of color and removal of other organic substances (expressed as BOD or COD) were shown to be possible with the use of a two-stage biological process. In the first stage, an anaerobic fixed-bed filter was used. The anaerobic filter was followed by an activated sludge process (Figure 3). During a 6-month period of investigation, very similar treatment effects were obtained. In Figure 4, an example of BOD and COD concentration of the influent and effluent from the anaerobic filter and aeration tank is shown. With a COD removal rate of about 37% from the anaerobic filter, the overall removal rate was about 80% in the two stages.

The most important result of treatment was the high color removal rate. When the influent color was said to be 100%, the effluent from the anaerobic filter ranged from 70% to 86%, and the effluent from the aerobic stage was 20% to 40%. On the aver-

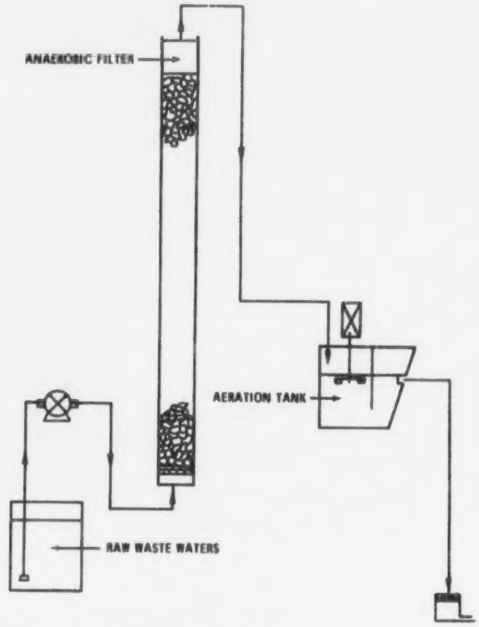

Figure 3. Scheme of the experimental units.

age, about a 25% color reduction was obtained during the anaerobic stage, but total color reduction was as high as 70% (Figure 5).

The anaerobic process used as the first stage resulted in structure changes of at least some dyes present in the mixture. To confirm these changes in dye structure, spectrograms in infrared and ultraviolet were done.

The use of an anaerobic filter as the first stage of biological treatment also results in an effective nitrification process in the activated sludge process. The anaerobic process leads to a distinct increase in the ammonia nitrogen content. The activated sludge process then resulted in nitrification of about 75% of the ammonia nitrogen to nitrates.

CHEMICAL TREATMENT

Effective treatment of combined municipal and textile wastewaters can be performed by the coagulation process. Chemical addition results primarily in high color and turbidity removal. Relatively good color removal can be obtained with simple lime addition. The effects of color removal vary with the concentration of dyes in the solution and the rate of added lime. Observations of 0.1% and 3.0% dye solutions in municipal sewage are presented in Figure 6. The characteristics of the sewage also seem to

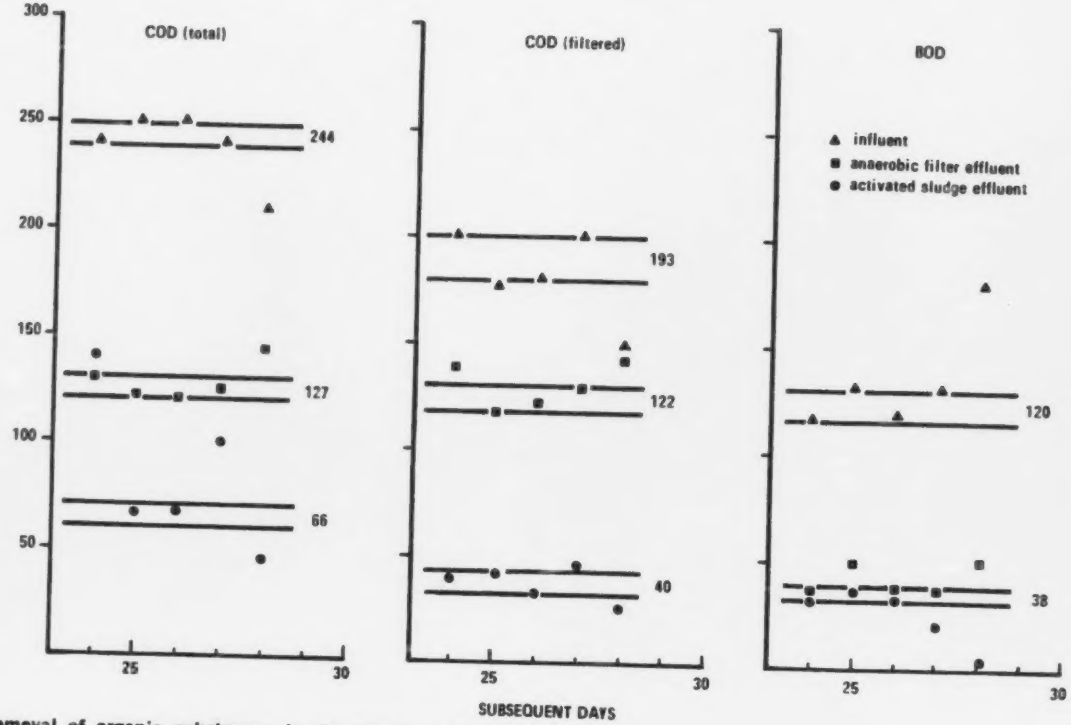

Figure 4. Removal of organic substances in the two-stage biological treatment process.

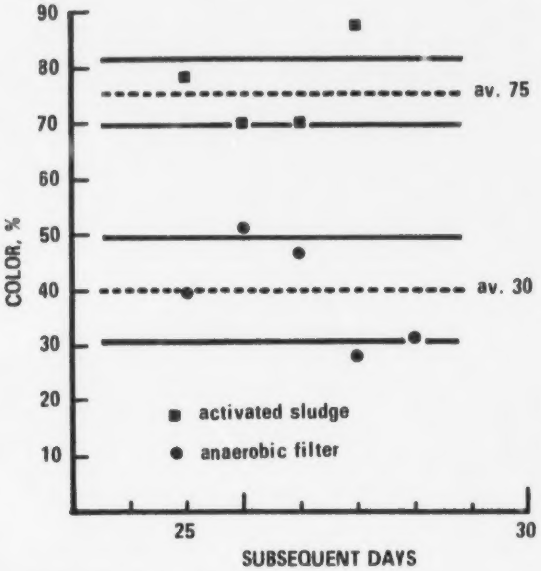

Figure 5. Color removal rate in the two-stage biological process.

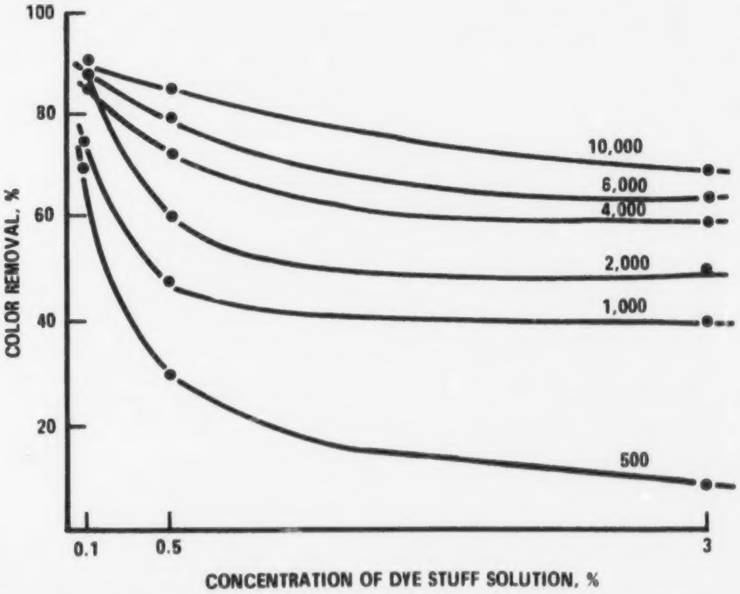

Figure 6. Effects of lime addition (milligrams CaO per cubic decimeter) on color removal.

have definite effects on the removal rate of the impurities. For example, data on color removal with the addition of 300 and 1000 mg/l CaO, given in Figure 7, are much higher than those presented in Figure 6. However, to be on the safe side, lime should be added in amounts of 4 to 10 g/l of CaO.

Figures 7 and 8 show that only large amounts of chemicals can assure high rates of color removal. As with lime, additions of copperas or alum does not improve the removal efficiency. An exception is the saturation with CO_2 after lime addition and sludge removal. The advantages of that procedure are not only color removal, but also an effluent pH close to 7. The coagulation process results in a reasonable removal rate of COD—10% to 50%. But a side effect of the process is the production of relatively large quantities of sludge. About 4 kg/m^3 of sludge with an average water content of 90% is produced. Depending on the wastewater flow to be treated, the sludge disposal problem can create a severe problem. When the process of recalcination is introduced, the sludge problem can be somewhat diminished.

ADSORPTION

Final removal of pollutants can be performed with the use of activated carbon. The use of the adsorption process for color removal has a long history, and thus much research has been done. Although some rules are well known, investigations are necessary in each specific case to obtain information on the capacity and kinetics of substance removal by activated carbon.

To get comparable results and characteristics, the adsorption capacity of powdered activated carbon was obtained for phenol in a 0.1% solution. The adsorption isotherm for phenol is given in Figure 9. Instead of phenol, COD determinations were performed to obtain comparable data on dye removal from prepared solutions. The determined capacity was about 160 mg phenol/g of activated carbon. Adsorption isotherms for seven different dye solutions are also given in Figure 9. Adsorption characteristics for the metals complex and basic dyes were similar to phenol. Relatively good adsorption was also noted for the reactive and acid-chromic dyes. The use of activated carbon as the final polishing stage after chemical precipitation provided total color removal. With color removal for the coagulation process in the range of 70% to 90%, an effective color removal through adsorption still requires about 1.5 g of powdered activated carbon per liter, with a minimum retention time of 30 min. It was interesting to learn that activated carbon capacity differed with the chemical used for coagulation (see Figure 10). The fine, unsettled suspension that remained after a 2-hr sedimentation period was probably responsible for this effect. Therefore, it is important to have a prefiltration step in advance of activated carbon.

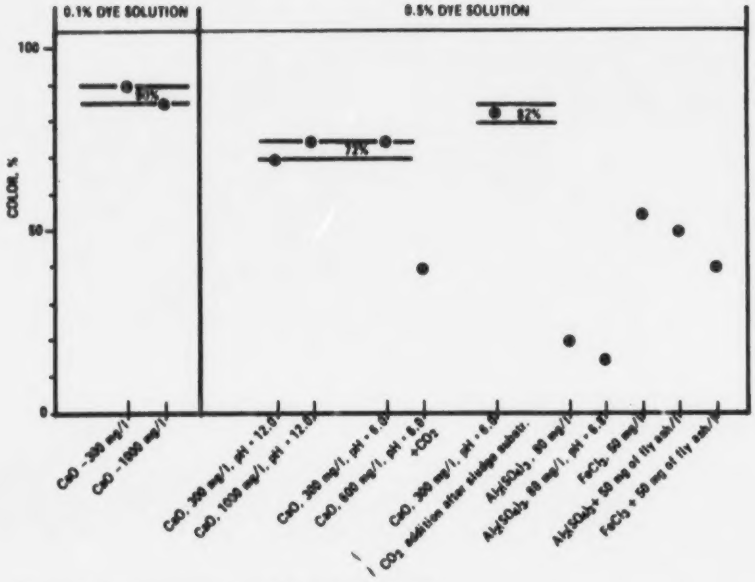

Figure 7. Color removed by different chemicals.

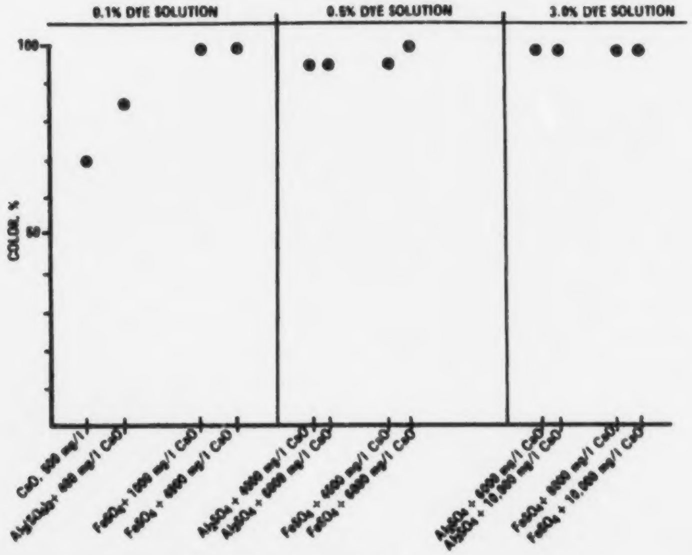

Figure 8. Color removed by different chemicals.

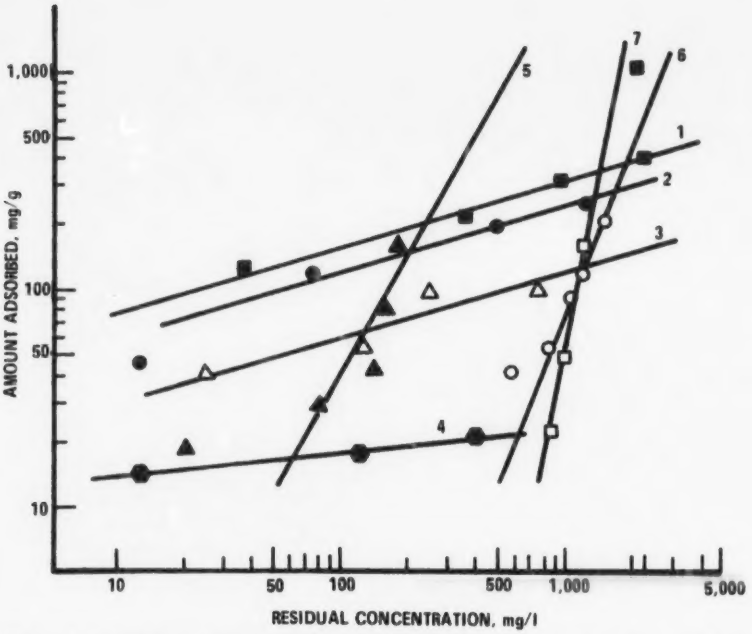

Figure 9. Adsorption isotherm. COD removal from phenol and dye solutions. Note: 1, phenol, 0.1%; metallic complex dye; basic dye; reactive dye; direct dye; suspended dye; and sulphuric dye.

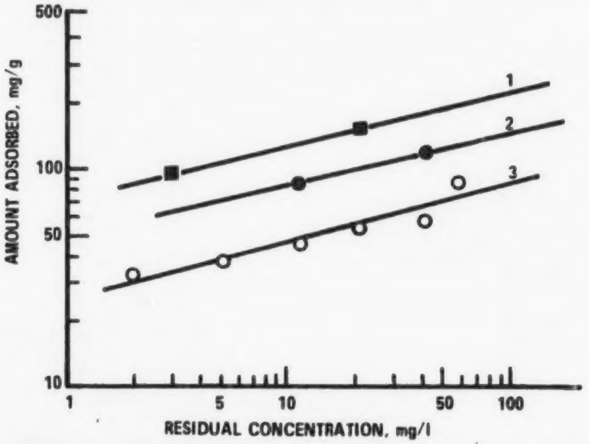

Figure 10. Adsorption isotherm. Color removal from chemically treated wastewaters. Note: 1, after coagulation by $Al_2(SO_4)_3$; 2, after coagulation by $FeSO_4$; 3, after coagulation by CaO.

TEXTILE WASTEWATER TREATMENT METHODS SUITABLE FOR RECOVERY

John J. Porter

ABSTRACT

The treatment of textile wastewater today is accomplished predominantly by biological waste treatment systems. This method of treatment is successful when the waste is biodegradable, as is the case with domestic wastewater. Since many industrial chemicals are resistant to biological degradation and have significant value, it may be better to use a waste treatment system that recovers these chemicals for reuse in the plant. A comparison of biological, chemical, and physical treatment methods is made, and the combination of these systems into a waste recovery process is presented. Reverse osmosis can play an important role in the recovery of chemicals, water, and energy.

When a waste treatment plant was designed and built in the past, it was assumed that it would adequately handle the waste stream with no more than minor revisions for some years to come. Today this assumption may not be entirely valid as far as conventional waste treatment plants are concerned.

The public is becoming increasingly aware of the known problems that pollution can cause, and they are apprehensive about unknown problems that have not yet been identified. Both of these factors have caused the enactment of new laws and regulations that have placed higher standards on outfall waters that enter natural streams.

In 1972, Public Law 92-500 was passed.[1] The objective of the "Act" is to restore and maintain the chemical, physical, and biological integrity of the Nation's waters. A national goal was set to eliminate the discharge of pollutants into navigable waters by 1985. A national policy was set to prohibit the discharge of toxic pollutants in toxic amounts.

With such regulations, it is no wonder that manufacturers are hesitant to install waste treatment systems that are obsolete before they are built. The comparison of waste treatment processes such as biological treatment, carbon adsorption, reverse osmosis, and chemical coagulation will be presented, and the integration of all processes into a design most likely to give zero discharge will be proposed.

BIOLOGICAL TREATMENT

Biological treatment of an industrial waste stream is successful if the waste stream is biodegradable. Sometimes the waste stream may be very biodegradable, other times it is not. The characteristics of six different textile waste streams are presented in Table 1.

TABLE 1. CHARACTERIZATION OF CONCENTRATED WASTE FROM SIX TEXTILE WASTE STREAMS

Constituent*	Wunda Weve	McCor-mick	Granite-ville	Green-wood	Springs Mills	Bishop
COD	2,500	3,720	15,285	4,032	8,871	2,596
Filtered COD	......	....	....	....	7,942	2,487
TOC	935	1,410	5,753	707	4,140	1,606
BOD_5	270	1,078	1,547	561	3,745	860
BOD_{10}	415	1,600	2,200	300	4,800	925
BOD_{15}	515	1,800	3,500	475	4,450	1,175
BOD_{20}	560	1,600	4,500	700	4,700	1,100
BOD_{30}	820	2,200	5,000	425	3,000	450
Solids:						
Total	3,760	5,028	10,028	9,870	8,702	4,334
Dissolved	3,000	4,803	9,853	9,785	8,347	4,106
Suspended	760	225	175	85	355	228
Volatile	2,030	2,104	4,050	1,254	5,074	1,714
pH	6.7	6.0	6.6	6.8	7.0	5.0
Color (Pt-Co units)	1,250	1,000	12,044	2,618	5,618	1,826
Turbidity (FTU)	43	3	opaque	0.38	opaque	15
Conductivity	2,000	3,900	9,000	9,600	5,000	4,000
Alkalinity	140	456	587	182	341	65
Hardness	32	57	74	135	75	97
Ammonia nitrogen	24	5	3	3	4	12
Total Kjeldahl nitrogen	25	11	6	6	10	14
Phosphorus	160	4.2	15	6	41	3.0
Phenols	1.0	0.40	0.52	0.1	0.1	0.1
Metals:						
Calcium	2.4	4.0	2.1	5.9	3.7	8.5
Chromium	0.13	0.19	8.1	3.1	1.4	......
Copper	0.2	1.2	8.6	0.64	0.66	6.2
Iron	1.3	1.3	10.3	12.0	7.0	2.9
Magnesium	1.0	6.0	12.0	13.0	24.0	......
Manganese	0.53	0.08	0.28	0.4	1.8	0.27
Mercury (ppb)	......	6.0	......	5.5	6.0	1.0
Nickel	0.33	0.17	1.2	1.9	0.1	0.56
Zinc	2.9	3.4	5.2	5.0	3.0	20.0

* Unless otherwise indicated, all units are in mg/l (ppm) (except pH).

These are waste concentrates taken from a pilot study of reverse osmosis conducted for the South Carolina Textile Manufacturers Association by Clemson University. The results of biological treatment are presented in Table 2. These results may be compared to general removal efficiencies of different treatment methods shown in Table 3.

It is evident that when the BOD_5 after treatment is compared to the COD (complete chemical oxidation), approximately two-thirds of the waste is degraded biologically in a 10-day retention system. The remaining portion of chemical constituents may be removed with the sludge in an activated sludge treatment, or pass through the plant untreated. The total removal of chemical constituents from the waste stream by a biological process is 66%. This rate is very good as biological processes go, but it is hardly good enough to meet the zero discharge required by Public Law 92-500 in 1985.

These data were obtained from a laboratory waste treatment system operating with a 10-day retention time in a mixed reactor (Figure 1). Nutrients, flow, activated sludge temperature, and dissolved oxygen are carefully monitored. A full-scale waste treatment system such as this should cost 50¢ to 70¢ per 1000 gallons to install, but as the data in Table 2 show, it would remove only 20% of the color-bearing constituents in the waste stream.

It seems reasonable to expect that conventional biological treatment as we know it today will not meet 1985 zero discharge requirements if they are enforced.

CHEMICAL TREATMENT

Coagulation

The use of chemicals to treat industrial waste can be very successful when they are used on specific waste streams. Pigments, latexes, phosphates, and many other suspended materials can be removed from industrial waste by simple coagulation. The coagulating chemicals that are used include alum, iron chloride, lime, and many organic polymers.[2] The preferred techniques vary and depend on the waste.

Temperature, pH, and total dissolved solids all affect the success of the treatment. If a waste stream requires specific coagulating conditions in the laboratory to obtain satisfactory results, coagulation may have limited success in plant operation if the conditions of the stream are constantly changing. For this reason equalization basins at the start of waste treatment plants may be necessary. The equalization basin will normalize the composition of the waste stream, and, if required, allow treatment chemicals time to react to give more stable sludges for separation. The design engineer may not appreciate the time it takes for lime or alum to completely react and form stable precipitates. It is very important that the sludge be stabilized if it is to be subsequently dewatered or agglomerated with organic polymers.[3]

TABLE 2. A SUMMARY OF OVERALL BEST RESULTS FOR TREATMENT METHODS
(% removal)

Item	Wunda Weve		McCormick		Graniteville		Greenwood		Springs Mills		Bishopville		Overall Av. % Removal	
	Before carbon	After carbon	Before carbon	After carbon	Before carbon	After carbon	Before carbon	After carbon	Before carbon	After carbon	Before carbon	After carbon	Before carbon	After carbon
Biological study:*														
% BOD_5 removal	85.9	97.4	89.0	92.0	39.0	36.2	95.2	99.1	98.3	99.3	97.2	95.4	84.1	86.5
% COD removal	43.7	72.4	59.7	62.5	28.7	35.1	33.3	88.0	64.8	65.7	64.0	62.7	57.3	64.4
% color removal†	16.4	56.4	0	0	0	0	27.0	51.3	75.2	75.7	0	0	19.7	30.5
Chemical treatment (commercial alum, 500 ppm):‡														
% BOD_5 removal	9.2		27.0		14.0		60.0		15.4		38.3		27.3	
% COD removal	9.6		23.0		23.0		78.0		13.9		45.4		32.2	
% color removal†	0		9.0		0		76.0		48.2		65.2		33.0	
Activated powdered carbon treatment (500 ppm):§														
% BOD_5 removal	61.2		29.2		76.1		71.9		35.0		22.7		49.4	
% COD removal	72.7		18.7		69.0		59.6		32.0		52.0		50.6	
% color removal†	61.5		67.4		67.1		71.4		79.8		52.7		66.6	

* Removal data for the biological study were based on the overall treatment results for the entire study period including removal data both before and after 1000 ppm carbon addition to the reactor and represent removal of the listed parameters from the decanted sample compared with the raw concentrate feed.

† Color data represent unfiltered or "apparent color."

‡ Removal data for the alum treatment were based on the best overall treatment (500 ppm in all cases) and represent removal of the listed parameters from the decanted sample after floc settling compared with the untreated raw concentrate.

§ Data for the carbon treatment were based on the best overall treatment (5000 ppm in all cases) and represent removal of the listed parameters from a treated filtered sample compared with an untreated filtered raw concentrate sample.

TABLE 3. REMOVAL EFFICIENCY OF VARIOUS TREATMENT METHODS (%)*

Constituent	Biological treatment	Alum coagulation	Carbon adsorption	Reverse osmosis
BOD_5	70-95	50-70	60-95	80-98
COD	30-70	50-70	60-95	80-98
Solids:				
Total	5-10	5	10-30	70-98
Volatile	10-50	50	50-80	75-98
Suspended	30-90	80-98	60-90	95-100
Color	10-80	80-90	80-98	95-100
Alkalinity	10-20	0-20	5	80-95

* These results are ranges for several studies. The value in a particular case may vary from this range.

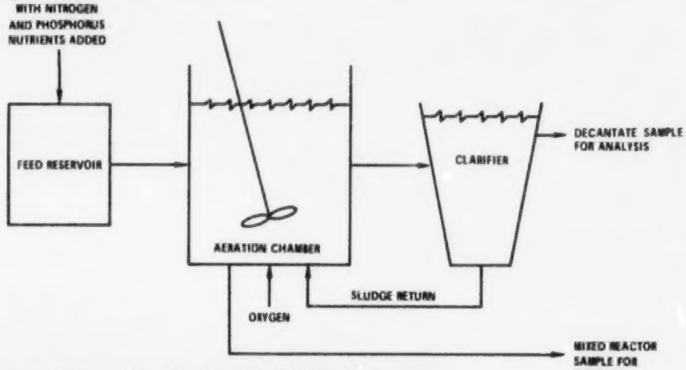
pH ADJUSTMENT
WITH NITROGEN
AND PHOSPHORUS
NUTRIENTS ADDED
FEED RESERVOIR
AERATION CHAMBER
CLARIFIER
DECANTATE SAMPLE
FOR ANALYSIS
SLUDGE RETURN
OXYGEN
MIXED REACTOR
SAMPLE FOR
ANALYSIS

Figure 1. Schematic of a batch-fed biological reactor.

The general treatment efficiency of alum treatment is shown in Tables 2 and 3. It can be seen that the total solids present in the waste stream decrease very little in most cases. This is because of the addition of soluble sulfate and neutralizing chemicals when the alum is added to the waste stream. If the treated waste is to be reused as plant process water, the sodium, chloride, or sulfate may build up to an intolerable range rapidly. In this case, reverse osmosis or ion exchange will be required to remove electrolytes.

Carbon Adsorption

Activated carbon has been used to treat many industrial waste streams for several years. It has the capacity to remove organic chemicals and dyes from the wastewater. Some transition metals may be adsorbed to a limited degree,[4] but more efficient processes such as ion exchange,[5] may be used for their removal.

Carbon will adsorb organic chemicals with limited water solubility from industrial waste streams.[6] Chemicals such as methanol, acetic acid, ethylamine, and ethylene glycol are not adsorbed significantly by carbon because of their high water solubility. Those which have very low water solubility, such as dye pigments, are not effectively adsorbed by carbon at room temperature. Chemicals with very large molecular weights, such as organic polymers, are not effectively adsorbed by carbon. That is to say, a small percentage of the chemical would be adsorbed from water after several hours at room temperature. In this case, it would not constitute a practical treatment method.

The only way the treatment of any waste stream can be assessed is by conducting laboratory and pilot plant studies to get good design data. The plant installing a new treatment system must be prepared to look into the future and accurately estimate what processes and chemicals will be used. If carbon adsorption is used as a treatment method, it must be as suitable for the future waste stream as it is for the present.

The average treatment efficiency for carbon adsorption is given in Table 3. If salts are a large portion of the total solids, their removal will be low. If the waste stream contains medium molecular weight organics, dyes, and detergents, it can be treated very effectively by carbon. The process must be carefully evaluated before the waste treatment plant is designed.

Reverse Osmosis

Reverse osmosis systems are defined for this paper as membrane-containing modules or units capable of rejecting low molecular weight salts, such as sodium chloride, to an efficiency of 30% to 98%. These figures are arbitrary, but they at least separate the membrane systems (ultrafilters) that are used to filter out colloids and polymers of molecular weights of 10,000 or better.[7] The spectrum of molecular sizes that are removed overlaps in theory and practice, so it is best to define the case for each study.

The other treatment methods (biological, coagulation, carbon adsorption) can be used to recover water, but they are not conventionally used to recover process chemicals from a waste stream. That is, biological treatment degrades part of the waste chemicals while contaminating the water containing them with a biological colloid. Coagulation contaminates the chemicals it can remove from the waste stream with an alum sludge, and carbon adsorption destroys the chemicals it removes from the waste stream when the carbon is reactivated at 1700 C.[6] (This is the common way carbon is used to treat industrial waste.)

Reverse osmosis, on the other hand, can isolate a product water of comparatively high quality and a concentrate water containing 80% to 95% of the chemicals present in the waste stream.[7] Data taken from an actual pilot plant operation are presented in Tables 4 and 5. The chemicals recovered here have been used in actual plant-scale dyeings.

TABLE 4. ANALYSES OF PRODUCT WATER OBTAINED BY REVERSE OSMOSIS TREATMENT OF TEXTILE DYE WASTE*

	Cycle number										
Constituent (ppm)	1	2	3	4	5	6	9	10	12	14	Tap water
COD	25	20	20	15	15	25	30	200	10	25	<4
BOD	10	5	5	4	0.3	1	2.7	1.3	2	1	0.6
TOC	3	4	4	4	4	......	......	......	......	5	4
pH	6.1	6.0	6.4	6.5	7.1	7.2	6.2	6.2	6.4	5.9	6.7
Alkalinity	10	15	15	15	25	15	40	3	10	8	27
Hardness	30	15	20	5	5	10	4	6	3	0.5	19
Total solids	100	270	130	280	440	285	630	215	230	50	67
Volatile solids	30	nd	20	40	40	60	95	75	65	15	36
Dissolved solids	100	270	130	280	440	285	630	205	230	50	59
Color (Pt-Co)	30	20	13	6	30	60	30	60	20	40	13
Turbidity (FTU)	2.4	0.5	1.3	0.8	3.4	6.3	1.5	6	2.0	2.5	1.11
Metals:											
Calcium	0.5	......	......	0.24	0.10	0.5	0.17	0.88	1.00	0.08	1.45
Zinc	<0.04	......	......	......	0.08	0.7	0.06	0.82	0.50	0.04	0.07
Mangnesium	<0.01	0.1	......	0.28	0.22	0.9	0.58	0.78	0.42	0.02	0.96
Chromium	......	<0.1	<0.1	......	0.1	......	......	......	......	0.10	<0.1
Copper	......	......	0.4	......	......	0.8	......	......	......	0.04	<0.04
Iron	0.04	<0.13	<0.1	......	......	......	0.63	1.13	......	0.14	<0.68
Mercury (ppb)	0.3	nd	0.56	......	......	......	......	......	......	......	2.51
Magnesium	......	<0.1	......	......	......	......	......	......	0.04	0.03	<0.05
Sodium	......	......	......	94	160	90	270	55	75	15	10

* La France pilot project sponsored by EPA.

TABLE 5. ANALYSES OF CONCENTRATED RESIDUES OBTAINED BY REVERSE OSMOSIS TREATMENT OF TEXTILE DYE WASTE*

	Cycle number										
Constituent (mg/l)	1	2	3	4	5	6	7	8	12	14	16
COD	425	815	455	580	690	435	190	415	365	430	255
BOD	70	135	60	102	95	10	15	45	15	20	55
TOC	87	200	110	165	220	......	......	......	......	230	100
pH	6.7	6.5	7.0	7.2	7.2	7.4	8.0	7.5	6.8	6.7	9.0
Alkalinity	110	135	110	160	190	140	155	115	95	160	250
Hardness	90	120	80	90	135	130	50	55	245	190	130
Total solids	2360	5570	2545	3020	4425	3425	1580	2510	4320	3025	3110
Volatile solids	200	450	280	310	405	315	165	275	245	275	......
Dissolved solids	2330	5540	2480	2985	4230	3435	1480	2450	4320	3025	3055
Color (Pt-Co)	850	1250	1500	1000	1200	1250	1300	1680	920	1100	190
Turbidity (FTU)	39	31	2	40	30	80	8	15	4	35	18
Metals:											
Calcium	3.0	......	......	6.5	9.0	6.0	1.0	8.1	34	7.5	11.5
Zinc	9.7	......	......	......	8.5	9.0	2.4	3.1	7.2	3.0	1.8
Magnesium	1.2	......	......	10.5	13.8	17.0	4.5	9.6	27.0	15.0	12.0
Chromium	......	<0.1	<0.1	......	0.1	......	......	......	......	0.6	......

* La France pilot project sponsored by EPA.

If the membrane is suitable for high-temperature operation, hot water can also be recovered. A flow scheme for conventional biological treatment is presented in Figure 2. A flow scheme illustrating how reverse osmosis may be attached to an in-plant process is shown in Figure 3. Here the wastewater from a specific process unit is treated before it is contaminated with other chemicals from other processes. The chemicals are recovered in their purest form most suited for reuse. The water and energy (hot water) can also be recovered for reuse. This system of direct reverse osmosis recovery at the in-plant point source can be applied to many plant processes. The process must be understood, and modifications in the process may be required before a reverse osmosis recovery sys-

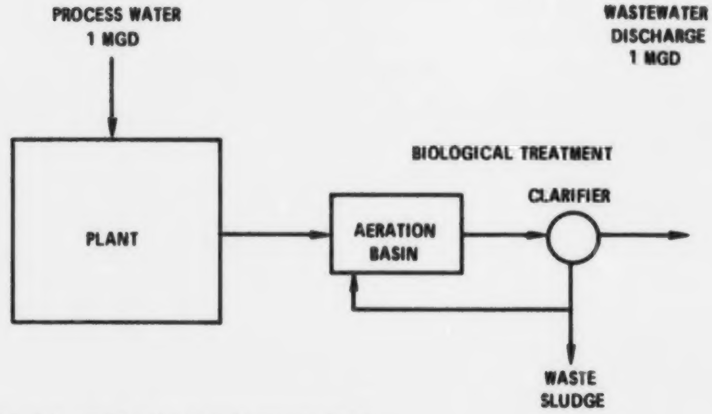
PROCESS WATER
1 MGD
WASTEWATER
DISCHARGE
1 MGD
BIOLOGICAL TREATMENT
PLANT
AERATION
BASIN
CLARIFIER
WASTE
SLUDGE

Figure 2. Plant using 1 mgd process water.

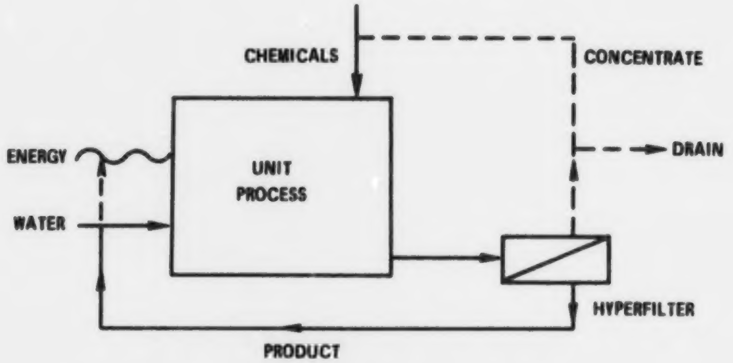
CHEMICALS
CONCENTRATE
ENERGY
UNIT
PROCESS
DRAIN
WATER
HYPERFILTER
PRODUCT

Figure 3. Recovery of water and chemicals at unit process.

tem is installed. The point is that if a chemical is recovered and reused, its original cost may be less important than the function it performs in the process. The stability of the chemical will (a) determine how many times it may be reused in the plant process and (b) indicate if degradation products with adverse effects on the process would be formed from its repeated reuse.

When reverse osmosis is used on a composite waste stream outside the plant, it may be used for all of the plant waste or part of the plant waste stream.

To get an idea of how this may compare with present technology, a diagram is shown in Figure 2 that illustrates the conventional biological waste treatment plant. All of the water coming into the plant each day is consumed in the process and becomes part of the manufactured product or ends up in the waste stream. The water must be purchased or manufactured by the plant. The waste stream must be treated before it is discharged. Present EPA regulations indicate that no pollutants will be allowed after 1985.[1] Since biological treatment only removes a fraction (30% to 70%) of the total organics in most industrial waste streams, it will have limited use in meeting 1985 standards. Although biological treatment will not be the complete answer to waste treatment in the next few years, it will play a very important part.

Chemicals that may not be treated with high efficiency by reverse osmosis, carbon adsorption, or chemical coagulation may be completely and effectively degraded by biological treatment. These include solvents such as methanol, acetone, glycol, methylamine, and formaldehyde. Other chemicals such as glucose or starch may be too unstable to be recovered and reused in a plant process. The plant would contain two outfall streams; one would contain chemicals that would go directly to a biological treatment plant for degradation, and another would go directly to a reverse osmosis treatment plant. Figure 4 shows how a plant would decrease its outfall from 1 to 0.1 mgd of sludge, which could be disposed of by spray irrigation and thereby eliminate a wastewater outfall altogether. This scheme will not constitute zero discharge in many

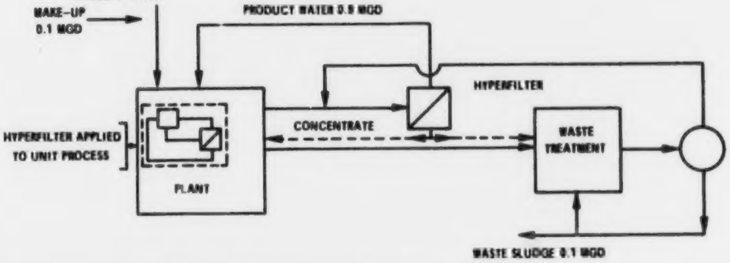

Figure 4. Integrated design; plant recovering 90% wastewater.

cases, as the sludge preparation for disposal may be significant, and thus a limiting factor. Another factor will be the buildup of dissolved solids in the process that recovers 90% of its wastewater. For example, if a plant uses process water of the general quality shown in Table 6 and recovers wastewater containing 1000 ppm dissolved solids, the plant adds a little over 900 ppm dissolved solids to the water passing through the plant. If 90% of the water is recovered and recycled as shown in Figure 4, the buildup of dissolved solids could be near 9000 ppm, a level that could make the treated water unsuitable for plant reuse. In such a case, close inspection of in-plant processes will need to be made to determine where salts may be eliminated from the process.

TABLE 6. ANALYSES OF FRESH WATER USED BY TEXTILE FINISHING PLANTS*

Constituent	Plant A	Plant B	Plant C
BOD_5	0	0	0
COD	5	2	6
Total solids	50	92	60
Dissolved solids	45	88	58
Suspended solids	2	4	2
Volatile solids	9	20	5
pH	7.5	7.6	7.8
Alkalinity	18	36	10
Hardness	3	8	12
Color	......	......	......
Phosphorus	0.1	......	......
Total nitrogen	0.6	......	......
Nitrate	0.3	......	......
Chloride	......	0.6	......

* All results reported in ppm except pH and color (Pt-Co units).

No doubt more worry would be involved for the plant manager, but such a system is a valid consideration for the future. A process chemical in the future will be chosen for its compatability with the waste treatment scheme, as well as its importance to the process. This appears to be the mechanism that will give society the desired increases in goods and services and at the same time protect the environment.

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REMOVAL OF REFRACTORY SUBSTANCES FROM TEXTILE WASTEWATER

Jerzy Kurbiel and Thomas N. Sargent

ABSTRACT

The U.S. Environmental Protection Agency (EPA) and the Polish Institute for Economy and Water Management (IEWM) are presently cooperating in an effort to investigate the effectiveness of selected advanced wastewater treatment processes. Combined, biologically treated, textile-municipal wastewaters are to be studied. The advanced processes include ion-exchange, carbon adsorption, chemical coagulation, oxidation, filtration, and reverse osmosis. The project plan calls for the investigation of the processes to be carried out singly and in combination.

The general approach to the investigations was to begin on the laboratory scale, then conclude on a pilot scale at the Andrychow Treatment Facility. The laboratory-scale work was performed at the IEWM facilities and the Krakow Polytechnic University in Krakow, Poland. Typical removals by mixed media filtration are SS, 60% to 80%; BOD, 3% to 60%; COD, 30%; and detergents, 20%. The results of the application of other processes are also given. (The data given are preliminary and subject to final verification and review at the termination of the project.) Reverse osmosis is the only one of the processes in which the actual pilot investigations have not begun. At present, the fabrication and installation of the reverse osmosis units are underway.

It is important to note the interrelationship of this PL-480-sponsored project and the current and future U.S. research program in textile wastewater treatment. No longer is it sufficient to remove only BOD and suspended solids. The current interests in industrial waste treatment are removal of refractory compounds by these and other advanced waste treatment processes.

RESEARCH OBJECTIVES

The U.S. Environmental Protection Agency (EPA) and the Polish Instytut Mateorologii i Gospodarki Wodnej (Institute of Meteorology and Water Management) (IMGW) are investigating the effectiveness of several advanced wastewater treatment processes on combined, biologically treated, textile-municipal wastewater. The textile industry discharges a wastewater that varies widely in physical and chemical characteristics, primarily because of the batch nature of their processing operations. The wastewaters are typically high in color and oxygen-demanding materials, are variable in pH, and may contain refractory (or difficult to remove by conventional treatment techniques) substances. These characteristics, together with previous studies on biological treatment, suggest that treatment by some processes other than, or in addition to conventional biological treatment is necessary for satisfactory treatment. In 1973, the EPA and the IMGW began the evaluation of ion exchange, carbon adsorption, chemical coagulation, oxidation, filtration, and reverse osmosis as tertiary treatment processes following conventional primary and secondary treatment. The investigations are being done on laboratory and pilot scale at the Krakow Division of IMGW, Krakow Polytechnic University, and the municipal treatment plant in Andrychow, Poland. The treatment investigations are scheduled to be completed in December 1976.

RESEARCH DESCRIPTION AND APPROACH

The Andrychow Cotton Textile Plant produces a variety of textile fabrics from a blend of cotton and synthetic fibers (70% and 30%, respectively). The whole yearly production amounted to 53 million m, or approximately 8.7 million kg.

The plant is divided into five departments: spinning, weaving, fiber dyeing, finishing "A", and finishing "B". The total yearly volume of water used within the plant is 2.02×10^6 m^3 (534×10^6 gal). The textile processing operations employ a wide variety of chemicals, including many types of dyes (reactive, vat, ice, indigosols, sulfuric, disperse), detergents, and alkalis (caustic NaOH).

The Andrychow wastewater treatment plant (Figure 1) treats wastewater containing municipal sewage and textile wastewaters.

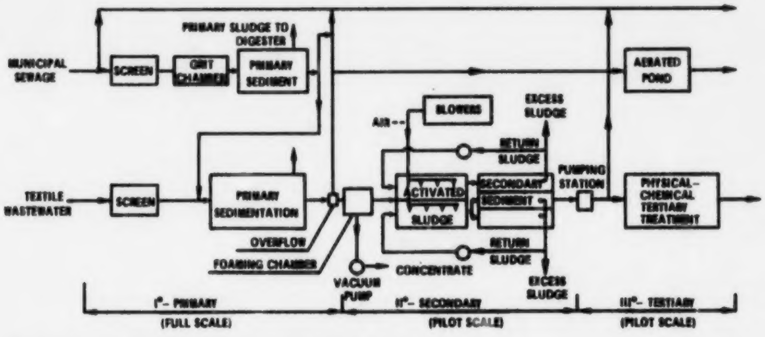
MUNICIPAL SEWAGE
SCREEN
GRIT CHAMBER
PRIMARY SEDIMENT
PRIMARY SLUDGE TO DIGESTER
AERATED POND
BLOWERS
AIR
EXCESS SLUDGE
RETURN SLUDGE
PUMPING STATION
TEXTILE WASTEWATER
SCREEN
PRIMARY SEDIMENTATION
ACTIVATED SLUDGE
SECONDARY SEDIMENT
PHYSICAL-CHEMICAL TERTIARY TREATMENT
OVERFLOW
FOAMING CHAMBER
VACUUM PUMP
CONCENTRATE
RETURN SLUDGE
EXCESS SLUDGE
I°- PRIMARY
(FULL SCALE)
II°- SECONDARY
(PILOT SCALE)
III°- TERTIARY
(PILOT SCALE)

Figure 1. Andrychow treatment plant flow diagram.

The primary portion of the plant treats a daily combined flow of 14,000 m^3. The secondary (activated sludge) pilot plant treats a daily maximum of 600 m^3. This secondary treatment provides the influent to the tertiary portion of the system. The tertiary processes (Figure 2) include rapid sand filtration (single or multimedia filters), granular carbon adsorption, chemical (alum) coagulation, ion exchange, oxidation with chlorine and ozone, and reverse osmosis. These unit operations are investigated in various combinations to evaluate the overall efficiencies. The scale of application of these tertiary processes and a more complete description is provided in the following text.

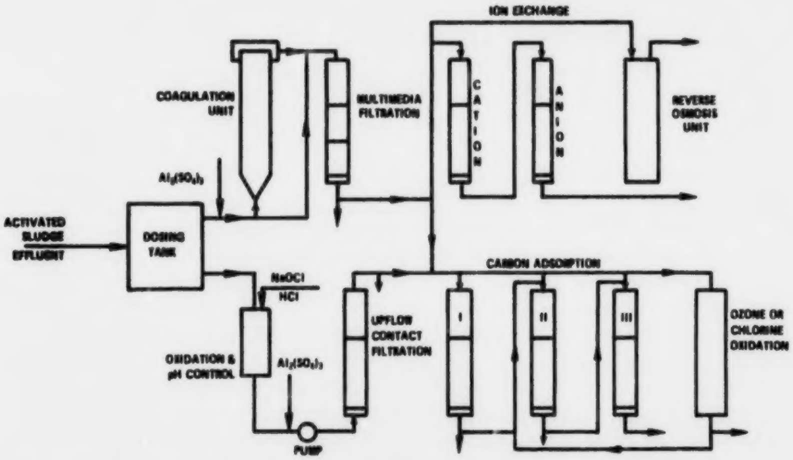
ION EXCHANGE
COAGULATION UNIT
MULTIMEDIA FILTRATION
CATION
ANION
REVERSE OSMOSIS UNIT
$Al_2(SO_4)_3$
ACTIVATED SLUDGE EFFLUENT
DOSING TANK
CARBON ADSORPTION
NaOCl
HCl
UPFLOW CONTACT FILTRATION
I
II
III
OZONE OR CHLORINE OXIDATION
OXIDATION & pH CONTROL
$Al_2(SO_4)_3$
PUMP

Figure 2. Diagram of tertiary physical/chemical processes at Andrychow pilot plant.

At present, a volumetric proportion of municipal sewage and textile wastewater during dry weather flow approximates 1:1.

Municipal sewage is characterized by rather low BOD_5 concentrations, ranging between 100 and 300 g/m^3, with an average of 170 g/m^3 O_2.

Flow and concentration of textile wastewater undergoes considerable fluctuations both during a day and a season. Concentration of pollution parameters in daily average samples are:

BOD_5	up to 660 g/m^3 O_2
Suspended solids	20 to 240 g/m^3
COD	100 to 700 g/m^3 O_2
Color	up to 1600 g/m^3 Pt
Detergents	14 to 110 g/m^3

In spite of pH control within the textile plant, the pH after pretreatment at the textile plant varies from 6.8 to 10.1.

The secondary effluent characteristics from the biological pilot plant that treats the combined wastewater are as follows:

Average BOD_5
removal 87%, with effluent concentration about 20 g/m^3 O_2
COD ....66% and 70 g/m^3 O_2
Detergents ....70% and 5 g/m^3
pH ....varies between 7.0 and 8.5

Of the heavy metals, 40% are removed with effluent concentrations less than 0.8 g/m^3. Average removal of color by biological treatment was 50%. Some dyes were not removed at all. Color concentration in the effluent was in the range of 20 to 160 g/m^3 (Pt units).

Tertiary treatment processes were investigated on the laboratory scale, followed in most cases by the second step study at the pilot plant. Laboratory tests were essential for preliminary assessment of the technical feasibility, selecting the mode of operation and range of technical parameters, or chemicals, involved. Because of the laboratory data and experience, it was possible to operate and manage the pilot investigations with optimized cost and time.

Rapid filtration on one or two media filters filled with sand and anthracite was conducted on both laboratory and pilot scale, mainly as a preliminary operation before another tertiary treatment process, or as a supplement to coagulation. The 150-mm-diameter columns were chosen for pilot scale after proof that this size had negligible wall effect.

Coagulation was studied as an independent process and is also being planned in combination with oxidation, carbon adsorption, and ion exchange. Pilot research included a conventional unit with flocculation and sedimentation compartments as well as a new concept of contact coagulation on filter. Supplementary laboratory jar tests to choose proper coagulants and their doses were performed.

Carbon adsorption experiments were conducted in two stages: first, laboratory tests to evaluate the adsorption properties of different granular carbons (including US Calgon and Polish Z-4 brand), and second, pilot investigations in 150-mm plastic columns to evaluate the effectiveness of organic refractory substances removal under continuous flow conditions.

The ion exchange process was also tested in two stages. Laboratory investigation allowed the researchers to select the most efficient ion exchange resins of both the cationic and anionic types in relation to color removal. A larger scale study applying continuous flow principles was conducted at the pilot plant scale.

Testing of the oxidation process was carried out intensively, first in the laboratory to prove technical feasibility of this process; pilot tests are to be performed later. Such oxidants as chlorine and atmospheric oxygen applied individually and with nickel and

UV light as catalysts were tested in batch laboratory experiments. The application of ozone was also evaluated. For further pilot plant research, chlorine and ozone were selected from the oxidants.

The Filtration Process

After the preliminary 1973 filtration investigations on a laboratory scale, the essential pilot scale research was started. Filtration metaplex columns were used with a 150-mm diameter and a height of 2.5 m.

The one-layer sand beds (granulation 0.5 to 1.5 mm, 1 m high) have been tested as well as the dual media beds consisting of anthracite (granulation 1.5 to 2.0 mm, 0.5 m high) and sand (granulation 0.75 to 1.5 mm, 0.5 m high). The hydraulic load in the range of 4 to 15 m^3/m^2/hr has been applied. Removal of contaminants in the following limits have been observed:

Suspended solids	60%-80%
BOD	30%-60%
COD	30%
Detergents	20%

The relative efficiency is primarily dependent on the concentration of suspended solids in the wastewater influent.

At the 1-m bed depth, no distinct influence of granulation or hydraulic loads on the efficiency of contaminant removal is apparent. For the shallower beds, a slight influence was noted.

The kind of bed, its granulation, and its hydraulic load have a basic influence on the value of the occurring head losses, the related length of the filtration cycle period, and the economic factors.

Previous investigations indicate that when a high degree of treatment is needed, filtration is worthy of recommendation as a tertiary process to be carried out after conventional biological treatment. Filtration is also applicable as a pretreatment for such processes as adsorption, oxidation, ion exchange, and reverse osmosis.

The Coagulation Process

In the coagulation process, contaminants are removed as a result of:

- —removal of the colloids,
- —generation of slightly soluble compounds (complex compounds and salts), and
- —sorption on the precipitated hydroxides.

Analysis of the applied dyes indicates that these dyes can be partially precipitated from wastewaters at a decreased pH value and an increased redox potential, and by coagulation.

The decreased pH value causes the increasing concentration of metal ions of the coagulant, which supports the precipitation of slightly soluble salts and complex compounds. The laboratory investigations have been performed on the influence of the lower pH value as well as on the increase of the redox potential on the elimination of color-yielding substances from the biologically treated wastewaters. The diminution of the extinction in the visible spectrum range is a measure of the treatment efficiency. Aluminum sulfate dosages from 100 to 600 mg/l were tried.

The mean percent of color reduction for six different wastewater samples at three pH values are shown in Figure 3. As can be seen from the curves, a decrease in pH has a positive influence on removal of color-yielding substances. The one-unit reduction of pH causes an increase in the mean color removal of about 25%. The influence of the application of NaOCl on the reduction of color-yielding substances is also shown.

In Figure 3, the coagulation of the wastewater samples is also presented at the same pH values but with a dosage of 8 mg/l of NaOCl. The positive effect of the oxidant combined with coagulation on the reduction of color-yielding substances is shown. At the higher pH value, the reduction increase amounted to 20%. Concentration of the compounds determined as non-ionic detergents amounts to a few mg/l.

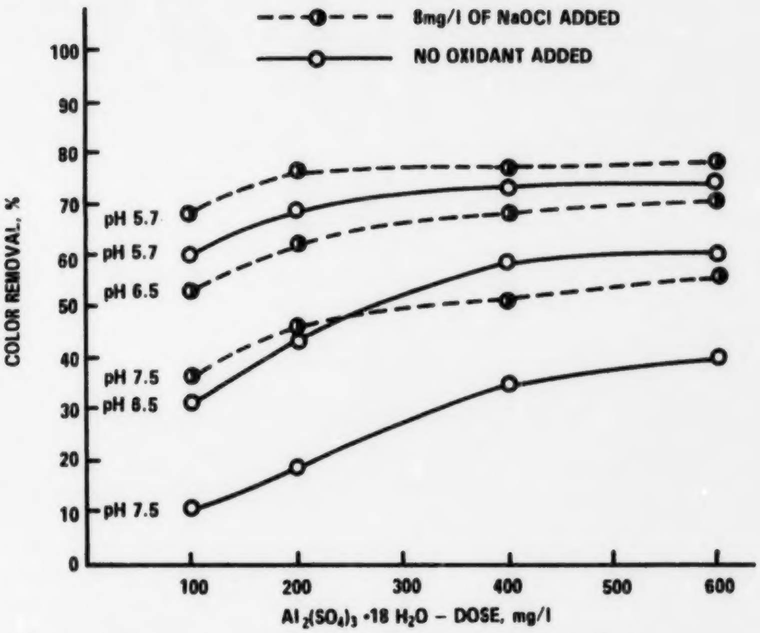

Figure 3. Influence of coagulant dose, pH, and chlorine preoxidation on color removal in biologically treated wastewater.

In the Andrychow pilot plant, investigations were carried out concerning the treatment possibilities of the combined municipal-textile wastewater after activated sludge treatment by coagulation with $Al_2(SO_4)_3$.

The coagulation process has been carried out at the same time in two technological systems:

- —with a simultaneous upward filtration through a sand bed, and
- —in a reaction chamber (with suspended flocs) followed by filtration through an anthracite sand bed.

The 150-mm-diameter coagulation columns have contact with the following layers of materials from the bottom up:

Gravel	0.4-4 mm, height 0.15 m
Sand	1.2-2 mm, height 1.50 m
Sand	0.4-8 mm, height 0.15 m

The suspended flocs reaction chamber has a diameter of 300 mm. The height of the flocs layer amounts to 1.5 m.

The filtration column, working in combination with the reaction chamber, was filled with two layers:

Anthracite	0.12-2 mm, height 0.5 m
Sand	0.4-0.8 mm, height 0.5 m

A dose of about 200 mg/l of $Al_2(SO_4)_3 \cdot 18\ H_2O$ was applied.

Contact coagulation was carried out at a rate of about 2.0 $m^3/m^2/hr$. The whole filtration cycle lasted about 24 hr. Wastewater pH was decreased by application of hydrochloric acid. The average results from a 3-week period are listed in Table 1.

To compare the influence of increasing the redox potential before the process of contact coagulation, 10 mg/l NaOCl was added. In the same series, the pH value was decreased as well by adding hydrochloric acid (Table 1).

Investigations of the suspended flocs system and coagulation followed by conventional filtration have been performed.

The average rate of flow in the reaction chamber amounted to 2.0 $m^3/m^2/hr$. The rate of filtration through the anthracite sand bed amounted to about 6 m/hr. The average results are given in Table 1.

DISCUSSION

In the contact coagulation process, a positive influence of the decrease of wastewater pH on removal efficiency has been determined. At a decrease in pH 7 to 5.7, the average color removal rate increased 16% and COD removal increased 20%. When coagulation was carried out in an identical system but preceded by oxidation, color and COD removal rates at the same pH increased 18% and 25%, respectively. The influence of oxidation on the amount of the COD and color removed by the application of 200 mg $Al_2(SO_4)_3 \cdot 18H_2O$ was considerable.

TABLE 1. EFFECTIVENESS OF PILOT PLANT COAGULATION PROCESS PERFORMED IN CONTACT UPFLOW FILTERS AND CONVENTIONAL UNIT

Item	Concentration of constituents in activated sludge effluent, pH 7.9	Activated sludge effluent after pH control and coagulation with 200 mg/l $Al_2(SO_4)_3 \cdot 18\ H_2O$					
		At pH 5.7		At pH 6.4		At pH 7.0	
		Concentration	Removal, %	Concentration	Removal, %	Concentration	Removal, %
Effect of contact coagulation alone:							
Suspended solids, mg/l	43	18	58	9	79	15	63
COD, mg/l O_2	74	24	67	23	68	35	47
Color, mg/ Pt	64	25	61	29	54	35	45
Effect of contact coagulation combined with previous NaOCl oxidation, 10 mg/l:							
Suspended solids, mg/l	39	11	72	16	59	12	69
COD, mg/l O_2	90	19	79	31	65	41	54
Color, mg/l Pt	74	18	76	27	62	31	58
Effect of conventional coagulation followed by multimedia filtration—no pH control or NaOCl added:							
Suspended solids, mg/l	39	......	......	......	......	9	77
COD, mg/l O_2	30	......	......	......	......	36	60
Color, mg/l Pt	74	......	......	......	......	40	46

Volumetric coagulation with filtration at the same pH values achieved nearly identical removal rates. A 13% higher COD removal rate can be explained by the lower suspended solids content in the effluent.

The Ion Exchange Process

Pilot plant investigations of the ion exchange process were carried out in the following system (Figure 2). Wastewaters of an industrial: domestic volume ratio of 2:1 after biological treatment were directed through a sand filter to the cation exchanger (filled with ZEROLIT 325/H+) and then through a CO_2 degasifier to the anion exchanger (filled with AMBERLITE 40_1/a−). The resins evaluated in pilot scale were selected by laboratory investigations. The column loads equal 6 bed volumes (BV) per hour.

One ion exchange cycle has been carried out up to the exhaustion of the cation exchanger. The cation exchanger efficiency was monitord by alkalinity analysis of the effluent and the anion exchanger efficiency by means of controlling the Cl^- ion content in the effluent. The cation exchanger regeneration was performed with a HCl solution, whereas the regeneration of the anion exchanger, even though not entirely exhausted, was performed with a NaCl solution. The load of the beds during the regeneration amounted to 1.0 to 1.5 BV/hr.

Samples for the analytical process control were collected from:

—the wastewater effluent from the sand filter,
—the wastewater effluent from the cation exchanger filter, and
—the wastewater effluent from the anion exchanger filter.

The samples were taken every 4 hr, preparing one average sample from the whole cycle. Analyses for the following constituents were performed:

—alkalinity or acidity
—pH
—BOD_5
—COD (dichromate and permanganate)
—Cl
—color
—anionic and non-ionic detergents

The cycle time of the cation exchanger column, and simultaneously of the whole system, amounted to 24 hr (average). In the system described above, five ion exchange cycles have been carried out. Presently, the cation exchanger column has been disconnected, so wastewaters are passed directly to the anion exchanger column. Investigations were continued with increased loadings (12 and 18 BV/hr).

Ozone Oxidation

Laboratory ozone oxidation investigations carried out using batch tests have proved that removal of color differs for particular dyes added to biologically treated effluent. Removal rates ranged between 11% and 87%.

COD concentration decreased 30% to 40%; the anionic detergents were reduced 28% to 75%. TOC reductions during batch ozone oxidation ranged from 16.7% to 83.7%, depending on the kinds of dyes present in the solution.

Influence of contact time, type of dye solution, and concentration of dyes on effectiveness of oxidation has also been tested.

FUTURE PLANS

The main activity during the last year of the project (1976) is to put into operation the reverse osmosis (hyperfiltration) unit, the only process that has not yet been tested.

The pilot installation for reverse osmosis, which requires a supply of some sophisticated equipment (i.e., high pressure pumps and membrane modules), has already been designed for application of two process systems: conventional modules and dynamically formed membranes. Startup of complete installation is planned for April 1976 in the Andrychow pilot plant on combined municipal-textile wastewater after biological treatment. Further plans include testing the hyperfiltration on overall textile wastewater and finally on the separated wastewater from the dyeing process. This last approach evaluates reuse of both product water and concentrate.

The investigation performed in the last 3 years on laboratory and pilot scale have enabled the testing of various unit processes in view of their technical feasibility and effectiveness in removing refractory substances. Further investigations are planned at the Andrychow pilot plant to include testing of the combination of processes such as oxidation and coagulation, coagulation and adsorption, ozonation and adsorption, coagulation and reverse osmosis. These investigations will prove the interaction of the processes responsible for refractory substances removal and optimization of the treatment techniques.

EPA RESEARCH AND DEVELOPMENT STUDIES ON TEXTILE WASTEWATERS

Thomas N. Sargent

ABSTRACT

The U.S. Environmental Protection Agency (EPA) is active in the development and demonstration of technology capable of meeting the requirements and goals of the Federal Water Pollution Control Act Amendments of 1972 (PL-92-500). The research and development program includes domestic and foreign activities dedicated to this principle. EPA has provided approximately $3.4 million in research and development funds since 1968. The general scope of activities of the research and development program's industrial interface is presented.

The Environmental Protection Agency's (EPA) research and development program is now operating under the legislative mandates of the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500). These amendments have three principal discharge restrictions for all industrial point sources. Briefly, these are the implementation of "Best Practicable Control Technology Currently Available" (BPCTCA) by 1977, of "Best Available Treatment Economically Achievable" (BATEA) by 1983, and the attainment of "Zero Discharge" as a national goal by 1985. The effluent guidelines for the textile industry were published in the Federal Register on July 5, 1974.

The purpose of my paper is to present the EPA research and development activities for assisting industry to meet the requirements of the legislation. The basic research and development program began in FY 1968. From FY 1968 through FY 1975, EPA has funded 27 projects directed toward aiding the textile industry in the development of treatment technology. The total value of these projects is approximately $7.9 million, with EPA providing approximately $3.4 million. Included in the 27 projects were 9 grants to colleges and universities, 3 grants to trade organizations, 14 grants directly to industry, and 1 grant to the Polish IMGW. The scope of these grants has ranged from literature searches through bench- and pilot-scale research to full-scale demonstrations at textile manufacturing facilities. The processes investigated on bench/pilot or full scale have been involved with demonstrations ranging from basic biological treatment through advanced physical/chemical processes (hyperfiltration, for example).

The objective in the early part of the research and development program was either to develop and demonstrate new technology or to apply existing technology in an area where it had not been applied. The current program—that is, since passage of PL 92-500 and the development of the effluent guidelines—is directed toward establishing technology applicable to the BATEA category of the requirement, and especially to the technology areas where the "zero discharge of pollutants" goal applies. The most important part of this latter work is to develop and demonstrate water management/treatment techniques that have as an integral feature the recycle and/or reuse of the aqueous emissions and the materials in these aqueous emissions.

Let me illustrate with a case history that exemplifies the stress on reuse/recycle of the water and the "pollutants" in the water. EPA awarded a grant to LaFrance Industries, a division of Riegel Textile, in June 1972. The objective of this project was to demonstrate the application of hyperfiltration technology in treating the wastewaters from a textile dyeing and finishing plant. The investigations included the use of both conventional (cellulose acetate) and dynamically formed membranes. The resulting retentate and permeate from the membrane units were evaluated for their recycle and reuse potential in the dyeing processes. The membrane units were operated on the pilot scale, and the reuse evaluation of the retentate and permeate were done on a full-scale dye machine. The final report for this project is now in preparation. The preliminary evaluation of the system indicates that absolutely no problems were encountered in using the permeate or the retentate in the dyeing processes. A complementary effort to the LaFrance project is currently underway in Krakow, Poland. This effort is a part of the PL-480 program and is under the direction of Dr. Jerzy Kurbiel.

This project is typical of those directed to solving EPA's and industry's problem of cleaning up our Nation's waterways. However, the Agency does not stop at the completion of a research and demonstration project. In addition to the final report mechanism, EPA goes several steps further in seeing that the information gets to the user. Technology Transfer personnel, as a part of the research and development program, function as an intermediary between the researchers and the user community. The Technology Transfer office uses capsule reports and seminars as their primary communication vehicles.

The research and development program is also involved in other activities of EPA. Research and development professional staff have been actively involved in the effluent guidelines development efforts of EPA by serving as technical advisors to the EPA Effluent Guidelines staff.

In summary, the research and development arm of EPA is vitally interested in working hand in hand with our friends in domestic industry and in other countries to develop effective pollution control, or water management techniques, for the private sector.

TESTING OF BIODEGRADABILITY AND TOXICITY OF ORGANIC COMPOUNDS IN INDUSTRIAL WASTEWATERS

Jan R. Dojlido

ABSTRACT

The development of industry in the world and the growing production of new substances have resulted in the discharge of many organic compounds into surface waters. Some of them are biochemically resistant and may be harmful to humans using water produced from contaminated surface waters. A knowledge of the toxicity and biodegradability of the new organic compounds will enable the proper treatment technology to be applied.

The paper discusses various methods for determining the biodegradability of organic compounds. The long-term BOD test method is a good one for determining oxygen uptake rates and toxicity to microorganisms. Several classes of organics are discussed as to their effect on the biological treatment of wastewaters.

Preliminary results are given from studies on compounds present in wastewater from a plant producing artificial leather, "Polcorfam." Methylethylketone was found to be easily degraded and not toxic to microorganisms up to 800 mg/l.

INTRODUCTION

The development of industry in the world and the growing production of new substances have resulted in the discharge of many organic compounds into surface waters. Some of them are biochemically resistant and harmful to aquatic life. They can also be harmful to humans using tap water produced from the contaminated surface waters. These substances occur at very low concentrations undetectable by conventional analytical methods. For these reasons it is necessary to know the nature of these substances, their behavior, and their harmfulness in the aquatic environment. The methods for determining these substances are indispensable. Knowledge of their properties enables the elaboration of proper wastewater treatment technology, and in some cases it can lead to the conclusion that some harmful substances cannot be discharged into the receiving waters. The purpose of the research reported here is:

- —to evaluate simple methods for biodegradability testing of organic compounds
- —to determine the biodegradability of several organic compounds especially harmful to the environment
- —to develop a fast toxicity test for organic compounds
- —to determine the toxicity of several harmful organic substances and to establish permissible concentrations of these substances in the aquatic environment
- —to develop analytical procedures for the determination of chosen organic substances.

METHODS FOR BIODEGRADABILITY TESTING

There are many varied methods for the determination of biodegradability of organic compounds:

a. Determination of BOD process by dilution. This method is rather rarely used because it is labor-consuming and because results are of little use.

b. Manometric method of Sierp. The oxygen uptake of the wastewater is determined by the change of the volume of the air in a flask containing the wastewater sample.

c. Warburg's manometric method of the wastewater sample closed in a flask. Oxygen uptake is determined by manometric measurement of pressure changes of the air above the sample.

d. Static test described by R. L. Bunch.[1] The organic compound to be tested with addition of yeast extract and inoculum is incubated in an open flask under standard conditions. After a given time, a decrease in the concentration of the test substance is analytically determined.

e. Electrometric method. The sample to be tested is continuously stirred in a closed flask. Oxygen uptake is measured by means of an oxygen probe immersed in the sample. One of the apparatuses based on this principle is called ATA (aerobic treatability apparatus).[2] An example of the results obtained by means of this apparatus is presented in Figure 1.

f. Another method of BOD determination is by means of the apparatus known as the "Sapromat" type. Over the wastewater sample in a closed flask there is a constant concentration of oxygen produced by an electrolytic generator at the same rate as oxygen is used for the biochemical degradation of organics. The oxygen uptake, determined from the work time of the oxygen generator, is recorded every hour. A typical example of the inhibiting effect of the test substance on the BOD is presented in Figure 2.[3]

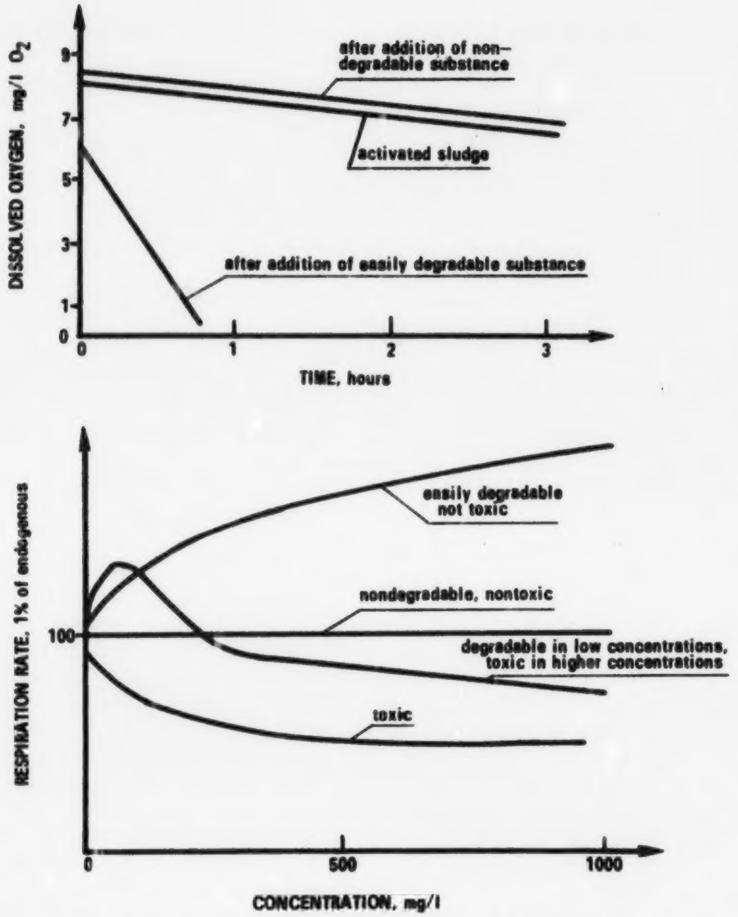

Figure 1. Typical curves showing stage of biodegradability of substances.

g. The laboratory-scale activated sludge model can be used for biodegradability testing. Descriptions of many such apparatuses can be found in the bibliography. One of them is described later in this paper. A schematic diagram is shown in Figure 3.

h. Simulated natural river conditions can be used for biodegradability tests. The simplest procedure uses an aquarium with the river water stirred at a rate similar to the turbulence in the river. The substance to be tested is added and analyzed at definite intervals. Also, constant flow-through types of apparatus are applied because they simulate the natural conditions much better.

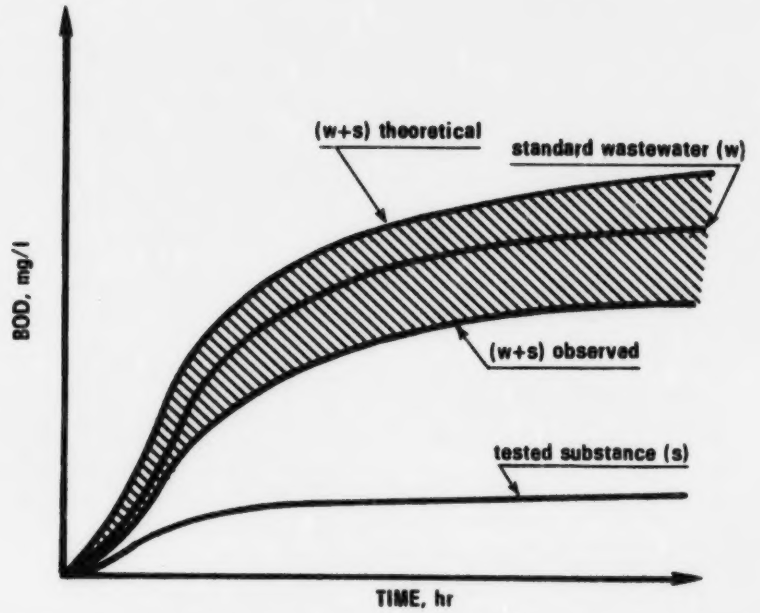

Figure 2. An example of the inhibiting influence of substances on BOD determined in Sapromat. If the observed curve (w + s) BOD is below the one for (w) BOD, the added substance is toxic. The area contained between the curves is the measure of the toxicity.

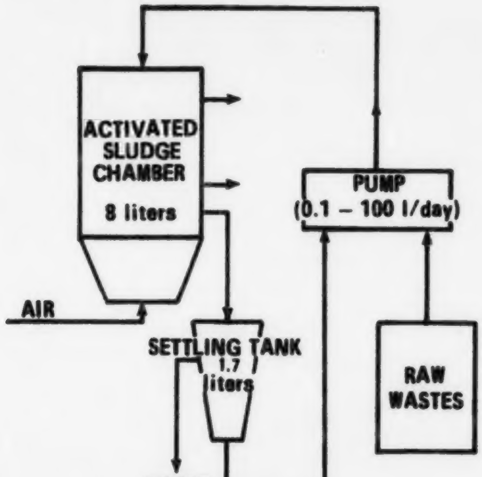
ACTIVATED SLUDGE CHAMBER
8 liters
PUMP
(0.1 – 100 l/day)
AIR
SETTLING TANK
1.7 liters
RAW WASTES
WASTE DISCHARGE

Figure 3. Laboratory-scale activated sludge system.

Analytical Procedures

In investigations on the biodegradability of organic compounds by the methods described above, some of the analytical methods used are BOD, COD, and TOC. However, analytical determination of the changes in test substance concentration during the biochemical process is the most advantageous. Usually in the biodegradability tests, pH value and the nitrogen forms content are measured. In the case of activated sludge testing, the sludge characteristics are also of great interest.

ORGANIC COMPOUNDS AFFECTING BIOLOGICAL TREATMENT OF WASTEWATERS

Hydrocarbons

These compounds are slightly soluble in water, so removing them from the water is rather easy. However, the tendency to form an emulsion of hydrocarbons and water can be troublesome. The hydrocarbons are slowly biodegradable. Biodegradability of these compounds is known to decrease with an increase in molecular weight and when the chain is longer and more branched. The toxic effect of the aliphatic as well as the aromatic hydrocarbons on the microorganisms of the activated sludge is observed at high concentrations (above 500 mg/l). Though hydrocarbons do not usually exhibit acute toxic effects, they can cause operating difficulties in biological treatment plants.

Alcohols

Most alcohols are easily biodegradable. Biodegradability decreases as chain length increases. Alcohol concentration in the inflow into the treatment plant is probably lower than 500 mg/l.[4] However, there are some alcohols of complicated structure that are hardly biodegradable—for example, polyethylene glycols and pentaerythritol.

Aldehydes and Ketones

The aldehydes undergo rapid biochemical decomposition if their concentration in the wastewater does not exceed 300 mg/l. the ketones are much more resistant to biodegradation. In the higher concentrations, the aldehydes and ketones have a toxic effect.

Carboxylic Acids and Their Salts

Carboxylic acids and their salts submit relatively easily to biochemical decomposition, and they do not disturb operation of the activated sludge treatment plants.

Phenols

Many phenols are easily biodegradable. In Poland,[5] several biological treatment plants effectively remove phenols from wastewater in concentrations of 1,000 to 2,000 mg/l. However, hydroquinone, which is toxic in concentrations above 500 mg/l, is somewhat resistant to biodegradation.

Halogen Derivatives

There is no accord among the results of biodegradability investigations on halogen derivatives made by different authors. Most of them have found these compounds resistant to biochemical decomposition. Biodegradability of aliphatic chlorinated hydrocarbons has been reported to increase when the chains are longer. The MCPB (metachlorophenoxy butyric acid) and 2,4-D (2,4-dichlorophenoxyacetic acid) are very resistant and have a negative effect on the wastewater treatment operation.[6]

Generally, introducing halogen atoms to an organic molecule significantly decreases the biodegradability of a given compound.[4] Such easily biodegradable substances as phenols and aniline or organic acids become difficult to biodegrade after introducing a chlorine atom to the molecule, and they are nearly nonbiodegradable after introducing two or more chlorine atoms to the molecule.

In addition, most chlorinated hydrocarbons are slightly soluble in water, and they easily form an emulsion in water.

Amines

The amines, aliphatic as well as aromatic, are biodegradable. Many authors consider the amine group as decreasing biodegradability of the molecule; for example, aniline is easily biodegradable, but the aminophenols and aminoaniline are slow to biodegrade.

Nitriles

Nitriles are easily biodegradable. The biodegradation of these compounds consists of hydrolysis to appropriate acids.

Nitrocompounds

The introduction of nitro groups to such aromatic compounds as phenols, amines, aldehydes, and acids decreases their biodegradability. The nitrocompounds have toxic effects on the microorganisms active in the process of biological wastewater treatment. Recently, a method of biochemical decomposition of nitrocompounds by the separate culture of *Azotobacter* has been discovered.

Sulphur-Containing Compounds

Among the compounds of this group, the detergents occur most frequently. Most of the investigators in the field of biodegradability have just dealt with the problem of detergent biodegradability. The alkylosulphates are the most easily biodegradable. Also, the alkylosulphonates, sulphonated amides, and alkyl esters are easily biodegradable. In case of ABS (alkylbenzenesulphonates), the rate of biochemical decomposition depends on the structure of the alkyl chain. If this chain is branched, the biodegradation becomes difficult and slow.

Other Organic Compounds

In addition to the above-mentioned organic compounds, many others can be found in industrial wastewaters—for example, carbohydrates, proteins, polymers, dyes, antibiotics, nonionic detergents, etc. Only a few of these compounds were investigated from the point of view of properties affecting biodegradability. Generally, it can be considered that the biodegradability of these compounds depends on the kind of functional groups present in the molecule, molecular weight, chain length, and chain branching. Still, information is lacking about the biodegradability and toxicity of many organic compounds. Those most frequently occurring in wastewaters from Polish industry are listed below:

a. Hydrocarbons—Crude oil, mineral oil, kerosene, gasoline, benzene, toluene, xylenes.

b. Alcohols—Methanol, ethanol, butanol, octanol, ethylene glycol, glycerol, cyclohexanol.

c. Aldehydes and ketones—Formaldehyde, acetaldehyde, acrolein, acetone, methylethylketone, cyclohexanone.

d. Carboxylic acids and their esters—Formic acid, acetic acid, propionic acid, palmitic acid, stearic acid, benzoic acid, salicylic acid, phthalic acid, terephthalic acid, acrylic acid, oxalic acid, methyl acetate, ethyl acetate, butyl phthalate, dimethyl terephthalate, methyl methacrylate.

e. Phenols—Phenol, cresols, xylenols, hydroquinone, pyrocatechol, alpha naphthol, beta naphthol.

f. Halogen derivatives—Chloroform, carbon tetrachloride, ethylene dichloride, trichloroethylene, tetrachloroethane, ethylene chlorohydrin, epichlorohydrin, chloroacetic acid, chlorobenzene.

g. Nitrogen-containing organic compounds—Dimethylamine, diethanoloamine, aniline, toluidine, triethanoloamine, ethylaniline, hexamethylenetetramine, diethylaniline, caprolactam, morpholine, dimethylformamide, cycloexylamine, acetonitrile, acrylonitrile, nitrobenzene, dinitrobenzene, dinitrotoluene, trinitrotoluene, pyridine, melamine, dinitrochlorobenzene, nitrophenols, dinitrophenols, picric acid.

h. Sulphur-containing organic compounds—Thiourea, mercaptobenzothiazole, benzenesulphonic acid, carbon disulphide, alkylbenzenesulphonates.

i. Other organic compounds—Nitrilotriacetic acid, methylcellulose, dioxane, diethylene glycol, triethylene glycol, trioxane, nonionic surfactants.

MATERIALS AND METHODS

In the project being conducted by the Institute of Meteorology and Water Management for the U.S. Environmental Protection Agency, the organic compounds considered most harmful for the water environment are tested. The most harmful compounds are considered to be those that are toxic, difficult to biodegrade, and present in industrial wastewaters at high concentration.

Materials

For the first part of the work, compounds present in wastewater from plants producing the artificial leather Polcorfam were chosen. The production of Polcorfam has started recently in Poland on the basis of a license bought from the DuPont Company. In the wastewater discharged from this production, the following substances are present and cause difficulties in treatment plant operation:

—methylethylketone (MEK)
—dimethylamine (DMA)
—dimethylformamide (DMF)

Methylethylketone— MEK (butanone-2), formula $CH_3COC_2H_5$, is soluble in water. This liquid, similar to acetone, is applied in many branches of industry, mostly as a solvent. In the production of Polcorfam, the recovery of MEK from wastewater by means of azeotropic distillation is applied, but recovery is not complete. So in wastewater discharged from Polcorfam installations, MEK is present at concentrations usually exceeding 100 mg/l.

Dimethylamine— DMA, formula $(CH_3)_2NH$, is a gas that condenses at 7 C (760 mm Hg) and is soluble in water. DMA is the homologue of ammonia, and it has similar chemical properties. Like ammonia, it forms complexes with Ag and Cu. In the weak acidic milieu, DMA reacts with nitrites to form nitrosodimethylamine, a suspected carcinogen.

Dimethylformamide— DMF, formula $(CH_3)_2NCHO$, is a liquid (boiling point about 150 C) soluble in water at every ratio. It is used in many branches of industry, mostly as a solvent. Under suitable conditions it easily hydrolyzes, forming formic acid and DMA. After the preliminary treatment, wastewater from Polcorfam production contains about 150 mg/l DMP.

Other substances to be tested will be chosen from the list given above.

Experimental Procedures

Long-term BOD Determination by Means of Sapromat Apparatus— The test sample, containing an inoculated solution of standard nutrient (yeast extract) and the added test substance, is kept in the flask of the Sapromat apparatus, fully saturated with oxygen and intensively stirred. Oxygen uptake is recorded every hour. One experiment consisted of BOD determination for the blank sample (yeast extract solution) and also for several samples containing increasing quantities of the test substance. The tests were continued for 20 days, and the solution reached its near-ultimate BOD.

Test Substance Decomposition Rate Determination by Means of Sapromat— The tests were conducted as described in the preceding section, the difference being that a portion of the same sample with a given concentration of test substance was introduced to all flasks in the apparatus. At regular intervals, a flask was removed from the apparatus and its contents analyzed for the test substance concentration.

Determination of Decomposition Rate of Test Substance in River Water— Water from the river receiving the wastes was tested in aquariums holding 20 liters each. To this continuously stirred water, a given amount of the test substance was added. The purpose of such a test was to simulate natural conditions. The decrease observed in the given substance concentration should be similar to that taking place in the receiving wastewater. The usefulness of such a test is limited if the test substance is volatile.

Determination of Effectiveness of Test Substance Removal by Means of Model Activated Sludge Test— A laboratory-scale activated sludge model can be used for simulation of the process occurring in the treatment plant. No fewer than two units in parallel must be kept in operation. The first is fed with standard wastewater, and the second one is fed with the same solution with the added substance. The effectiveness of the activated sludge process and the influence of the test substance on this process is determined by means of chemical analysis of influent and effluent concentration of the test substance, COD, NO_2, NO_3, volume index of activated sludge, and microscopic analysis of activated sludge.

Simple Static Test of Decomposition Rate of Test Substance in Standard Solution— The test substance in known quantities is introduced to the set of flasks inoculated with the standard nutrient solution. At regular intervals, the contents of a flask was analyzed for test substance concentration, COD, and nitrogen forms.

Toxicity Investigations

Toxicity of organic compounds to be tested was determined by means of acute toxicity tests. Static as well as dynamic (constant flow) methods were applied. The following organisms for the tests were chosen:

—*Daphnia magna*
—*Asellus aquaticus*
—*Lumbriculus variegatus*
—*Lebistes reticulatus*

Static Tests of Toxicity— These consisted of observation of behavior and reaction of test organisms over a 96-hr period. The test substance was added to 250 ml of water in open beakers. In tests of this kind, the chemical composition of the beakers' content changed because of biodegradation of the test substance and the accumulation of diverse products of metabolism.

Dynamic Tests— Dynamic tests were performed by means of a proportional diluter. This apparatus is the automatic device for continuous dilution of the test substance at the required ratio and for feeding the containers in which the test organisms were placed.[7] In this system, the test substance remains at the same concentration even during long-term tests, and the products of metabolism are removed continuously. Because the proportional diluter described[7] is equipped with open containers for test organisms, it is not suitable for experiments with highly volatile substances. A volatile study apparatus is described in the following section.

Apparatus for Testing the Toxicity of Volatile Substances—Some toxic substances are very volatile and may be a threat to the health of laboratory workers. Test results may also be affected by loss of volatile materials during the experiment. Thus a special apparatus was constructed to test the toxicity of volatile substances (Figure 4). Temperature is thermostatically controlled. Through the bottle containing the test organisms, a peristaltic pump forces a constant flow of 50 to 100 ml/min of oxygen-saturated fresh water containing the test substance. The concentration of the test substance is controlled by adjusting the pump. During the experiment, the test solution does not contact the atmosphere; and at the same time, the flow through the bottle renews the solution several times every hour, thus removing the products of metabolism. Observations of the test organism mortality are used to determine the LC_{50} by the graphic method or by computation, using the probits transformation.[7]

Analytical Procedures

Sensitive analytical methods are required to determine the test substance concentrations occurring in raw wastewaters, in the effluents from wastewater treatment plants, in surface waters, and at the concentration legally permissible in natural waters. Gas-chromatographic methods are often the best among the available procedures.

Determination of MEK

The gas chromatograph Pye-Unicam Model 1104 has been applied in our laboratory. The column is filled with Poropak Q covered with polyethylene glycol 1000 as a stationary phase. A flame-ionization detector is used, and the carrier gas is nitrogen. The direct injection of aqueous sample has been used, depending on the concentration range, or sample concentration can be

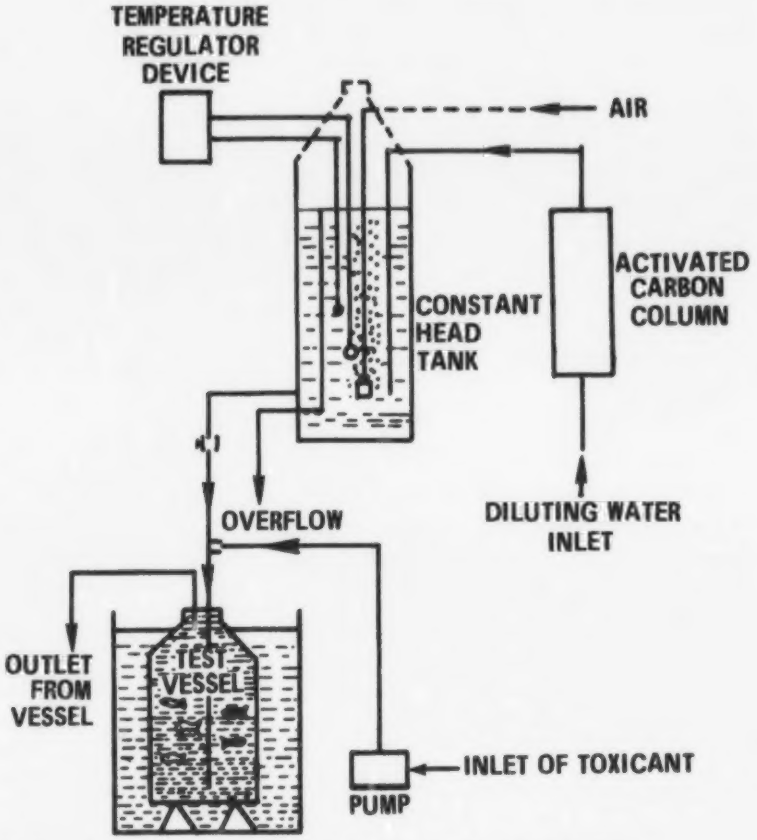
TEMPERATURE REGULATOR DEVICE
AIR
ACTIVATED CARBON COLUMN
CONSTANT HEAD TANK
OVERFLOW
DILUTING WATER INLET
OUTLET FROM VESSEL
TEST VESSEL
PUMP
INLET OF TOXICANT

Figure 4. Constant-flow apparatus for bioassay on volatile substances.

achieved by extraction of MEK by means of toluene using sodium sulphate as the salting-out agent. The lower detection limit is 0.1 mg/l.

RESULTS

Biodegradability Test Results for MEK

Long-term (17-day) BOD's— Long-term (17-day) BOD's were run in the Sapromat apparatus for six samples of MEK. The concentrations varied from 0 ot 800 mg/l. In addition to MEK, each sample contained 200 mg/l yeast extract in dilution water and 150 ml/l domestic wastewater, both of which were previously tested for their nontoxic and good inoculation properties. The BOD time curves were drawn on the basis of oxygen uptake printed records. Three of these curves are shown in Figures 5, 6, and 7. These graphs show that after initial lack of oxygen uptake (lag phase), the BOD curve is concave up to the inflection point, and further on it is similar to the monomolecular reaction curve. In the final part of the curve, two waves (probably caused by 1st and 2nd stage nitrification) are visible (Figure 6). It can be assumed that after the lag phase, the biochemical process, and thereby the oxygen uptake, is under the influence of exponential growth of bacteria. So the oxygen uptake rate should follow the equation:

$$\log \frac{dy}{dt} = c + b \cdot t$$

where

y = oxygen uptake, mg/l day
t = time, days, and
b = growth coefficient, day^{-1}.

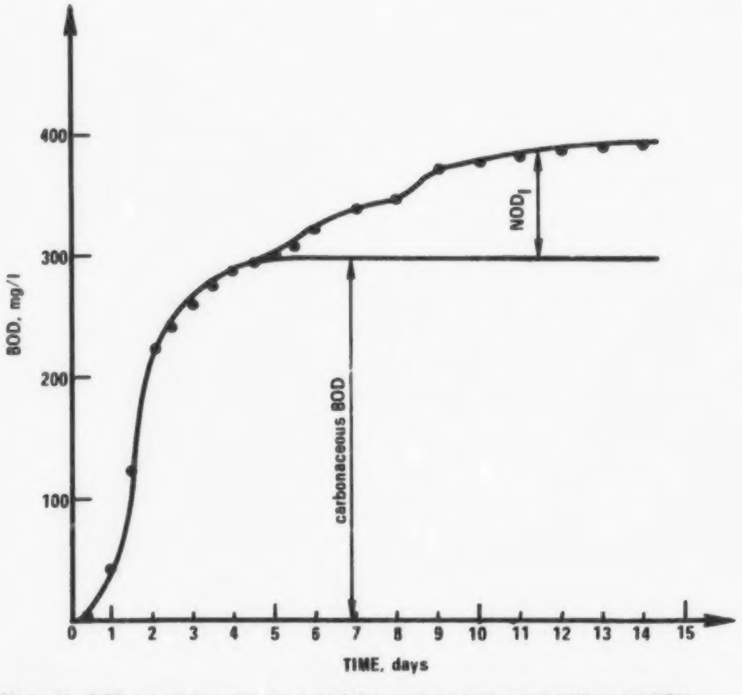

Figure 5. BOD curve for sample containing yeast extract and 100 mg/l MEK.

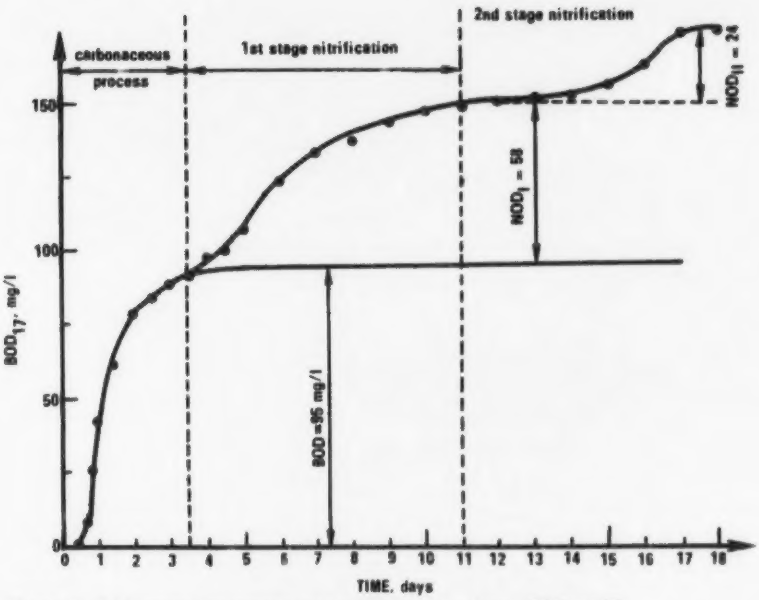

Figure 6. BOD curve for sample containing yeast extract (200 mg/l).

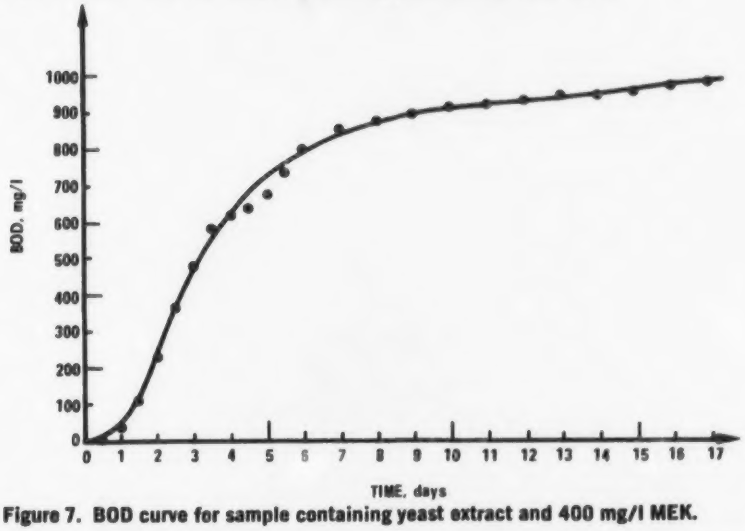

Figure 7. BOD curve for sample containing yeast extract and 400 mg/l MEK.

From the graphs made in coordinate system log dy/dt versus time, one can read out (see Figures 8, 9, and 10):

—time of lag phase duration, – t_0
—time of exponential phase ending, – t_1
—growth coefficient b (from the slope of the straight line)

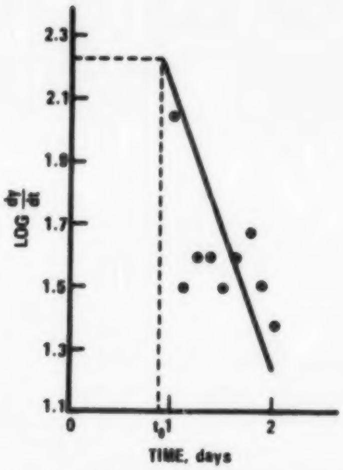

Figure 8. Oxygen uptake (control); yeast extract.

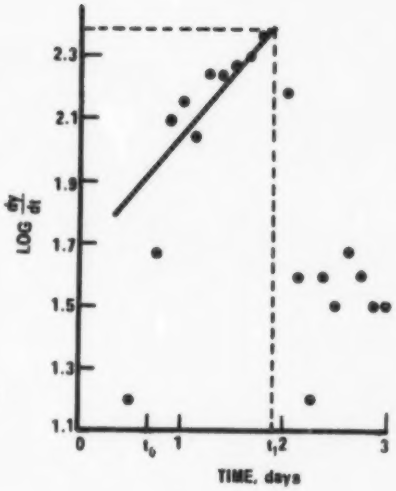

Figure 9. Oxygen uptake; yeast extract + 100 mg MEK/l.

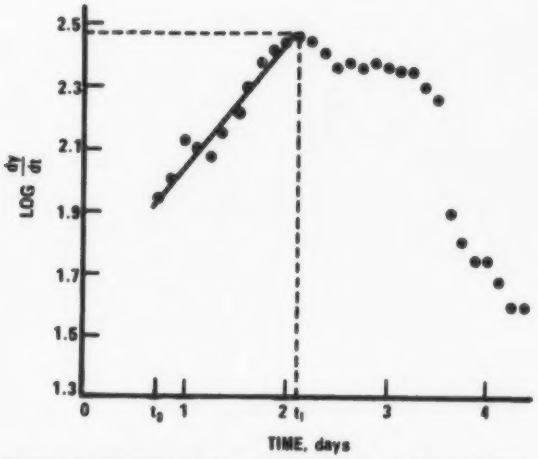

Figure 10. Oxygen uptake; yeast extract + 400 mg MEK/l.

The oxygen uptake results are shown in Table 1.

TABLE 1. OXYGEN UPTAKE RESULTS WITH MEK

Time	MEK concentration, mg/l				
	0	100	200	400	800
t_0, hours	14	14	14	14	14
t_1, hours	20	44	47	49	43
b, day^{-1}	n.d.*	0.38	0.46	0.40	0.46

* Not determined.

It has been assumed that in the next section, the BOD curve follows the monomolecular reaction equation

$$y = L/1 - 10^{-k_1 t}/,$$

where

L = final BOD, mg/l O_2
k_1 = coefficient, day^{-1}, and
y and t = as above.

The parameters L and k_1 can be calculated by means of the least squares method. The time of duration of carbonaceous process (monomolecular)—the period of time between the end of the exponential phase and the beginning of the first wave of nitrification—has been considered. After computation of k_1 and L for this section of time only, the oxygen demand for nitrification (NOD) in the first and second stage has been read out. A comparison of the first- and second-stage NOD readout from the graphs, with theoretical values calculated from the known ammonia and organic nitrogen content in the sample, has proved a mutual accord. At the higher MEK concentrations, the NOD could not be read out because of the small ratio of NOD to carbonaceous BOD. Results are presented in Table 2.

TABLE 2. BOD PARAMETERS FOR MEK

MEK concentration, mg/l	L_C,* mg/l O_2	NOD, mg/l O_2	k_1 day $^{-1}$	t_N† days
0	95	82	0.47	3.5
50	194	90	0.49	4.5
100	300	100	0.51	4.5
200	495	112	0.37	5.5
400	949	n.d.‡	0.17	15
800	1995§	n.d.	0.09	n.d.

* L_C denotes the final carbonaceous BOD.
† t_N is the time of the beginning of nitrification.
‡ Not determined.
§ NOD included.

From the L_C values, the total BOD of 1 g MEK was calculated by subtraction of the blank sample BOD from the BOD of samples containing MEK. The mean value obtained is equal to 2.1 g O_2, whereas the stoichiometric value amounts to 2.44 g O_2.

Examination of MEK Degradation in the Sapromat Apparatus— Six identical samples, each containing 200 mg/l yeast extract and 200 mg/l MEK, and inoculated with 150 ml/l domestic wastewater for the first experiment were incubated in the Sapromat and the BOD recorded. At regular intervals, usually 12 hours, a flask was removed and the MEK concentration was determined. The second experiment was performed, with the only difference being that the content of the last flask from the first experiment was used for inoculation instead of wastewater. The concentrations of MEK were marked on the graph versus the time (Figure 11). From the graphs, the long time of adaptation of microorganisms in the first experiment is visible, whereas the graph for the second experiment shows that adaptation time is significantly shorter. The MEK content in the first experiment does not show a significant decrease during the first 2 days, and BOD during this period is equal to the BOD of the yeast extract. In the second experiment, MEK degradation starts earlier, and the time required to achieve full MEK degradation is 2.5 days compared with 5 days for the first experiment.

The Static Tests— The tests were performed in hydraulically sealed bottles to avoid losses of MEK by evaporation. Over the surface of the sample a volume of air was left to permit reaeration of the sample. At regular intervals, the contents of a flask were analyzed for MEK and COD. Initially samples contained 50 mg/l yeast extract and 20 mg/l MEK. The samples in the first experiment were inoculated with domestic wastewater, whereas samples in the second experiment were inoculated with the last sample of the first experiment. Concentrations of MEK were marked on the graph versus the time (Figure 12). Microorganisms in the last sample of the first experiment were shown to be adapted to the MEK milieu, since in the second experiment, MEK degradation proceeded faster.

Examination of MEK Decrease in River Water— Tests were made in aquariums containing 20 liters of Vistula River water. In one aquarium, 20 mg/l MEK was used. The MEK decrease was drawn on the graph versus the time (Figure 13). The graph shows that after an adaptation period, the rapid degradation of MEK results in almost full decay in 2.5 days. Repeated addition of MEK to the same water has proved that river microorganisms were adapted during the first 2.5 days. To estimate MEK decrease resulting from evaporation, the control aquarium was filled with Vistula River water to which was added 20 mg/l MEK and biocide (50 mg/l $HgCl_2$). Analysis of the contents of this aquarium have proved that only a part of the MEK decrease was caused by evaporation.

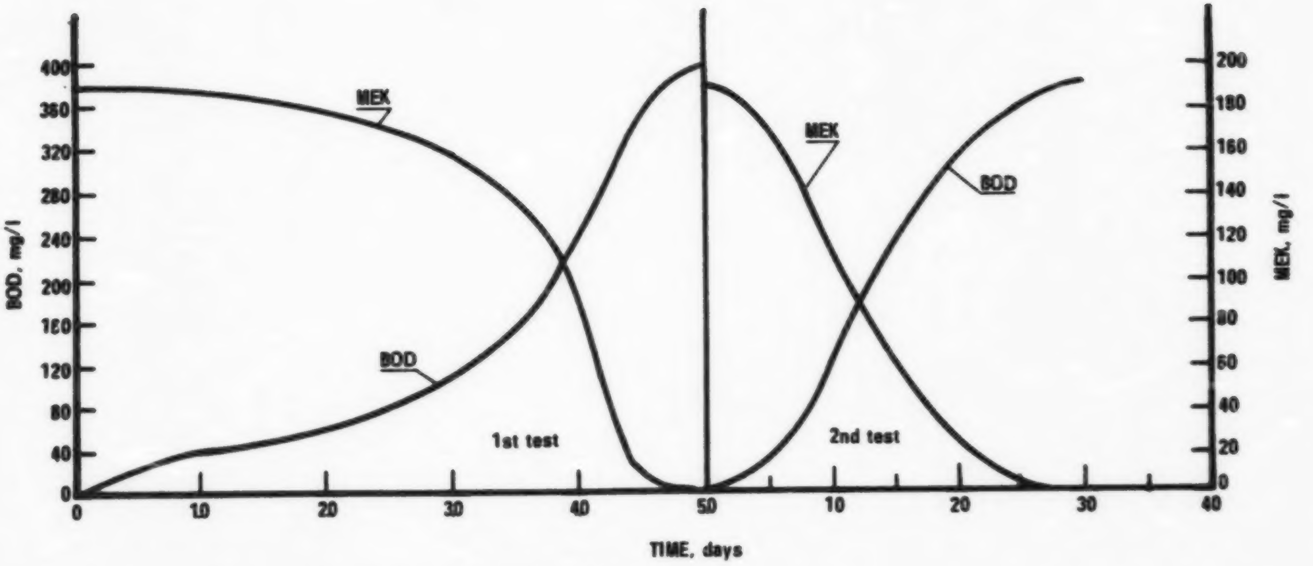

Figure 11. The test of MEK biodegradability in Sapromat apparatus.

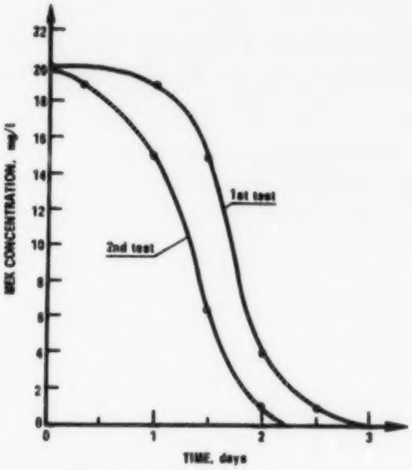

Figure 12. Decrease of MEK content during the static test of biodegradability.

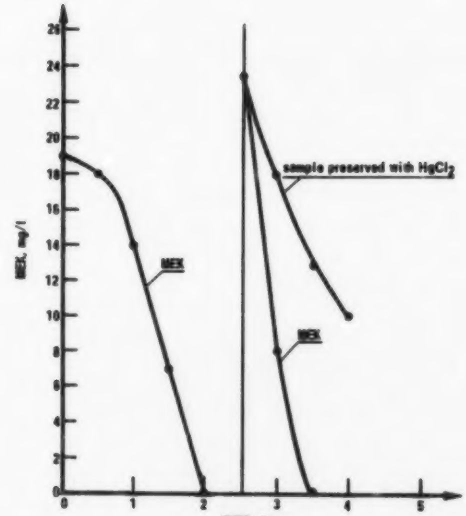

Figure 13. Decrease of MEK content in river water.

Toxicity Tests

MEK toxicity tests were performed as acute toxicity tests using the fish *Lebistes reticulatus* as the test organism (Table 3). Results show that fish tolerate relatively high MEK concentrations. First results showed that the LC_{50} for MEK after 24 hr equals 6 g/l. During the 96 hr of the experiment, the toxic effect has decreased, which can be explained by the degradation and evaporation of MEK from the test solutions kept in open beakers. Thus a specialized apparatus for determination of volatile substance toxicity was constructed for subsequent experiments (Figure 4).

TABLE 3. SURVIVAL OF *Lebistes Reticulatus* IN MEK SOLUTION (STATIC TEST)

	Number of survivors							
MEK concentration, g/l	15 min	30 min	1 hr	24 hr	48 hr	56 hr	72 hr	96 hr
Control	20	20	20	20	20	20	20	20
1.9	20	20	20	20	19	19	19	18
2.2	20	20	20	19	17	17	17	17
3.4	20	20	20	18	18	18	18	14
4.5	20	20	20	15	15	15	15	14
6.0	20	20	20	12	12	12	12	12
7.0	20	20	3	3	3	3	3	3
10.8	20	0	0	0	0	0	0	0

CONCLUSIONS

1. There is a lack of uniform, commonly used, simple, standard methods for determining biodegradability of organic compounds.
2. Available information about biodegradability of organic compounds is often divergent and difficult to generalize and apply in practice.
3. There is a lack of information about the occurrence of many organic compounds in surface water and about the harmful effects on biocenosis exerted by these compounds.
4. The method of biodegradability testing by means of long-term BOD curve examination has proved a good method for preliminary investigation, yielding such information as units of oxygen uptake, oxygen uptake rate coefficient, and toxicity to microorganisms. The method for measuring decay of the test substance gives additional information about the relationship between BOD and decrease in test substance concentration. The static test is a good method that can substitute for the former test in case of lack of Sapromat apparatus.
5. MEK is easily biodegradable and has no harmful effects on the sewage microorganisms at concentrations up to 800 mg/l. The

oxygen uptake rate coefficient k_1 amounts to about 0.5 day^{-1}, if the nutrients are in sufficient quantities. The rate of MEK biodegradability increases rapidly after the adaptation of microorganisms.

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CONCEPTS, CRITERIA, AND MEASUREMENTS OF BIODEGRADABILITY

Robert L. Bunch

ABSTRACT

Biodegradability has become a key word in the lexicon of everyone interested in the pollution problem. Why, suddenly, is there such interest in biodegradability? Traditionally, nature provided the ultimate disposal of manmade wastes, but as man advanced technologically, nature's work became more difficult. In fact, nature fails to degrade some of the newer manmade substances. Thus, the accumulation in the environment of many of the newer products synthesized by man and the advent of new legislation requiring pretreatment for wastes that are not removed by conventional wastewater treatment plants, has focused considerable interest on biological degradation or biodegradability. Some researchers prefer not to use the term "biodegradability" in connection with wastewater treatment processes; they favor instead the term "treatability."

Biodegradability has been defined in several ways. In the real world of wastewater treatment, the extent of biodegradation within a fixed time limit is a very important consideration. In principle, laboratory testing should show the true biodegradability of the test material as it would occur in the environment or in the wastewater treatment plants.

How biodegradable should a compound be? The possibilities range all the way from slight to ultimate breakdown of the compound to cell matter, carbon dioxide, and water. Biodegradability must be measured in terms of its effect on the environment. The future would indicate that the environmentally acceptable biodegradability criterion for products that become waterborne wastes should be that they are completely degraded to products that are harmless in surface and drinking waters.

This paper discusses in detail the definition and the various test methods for determining biodegradability. The important features, advantages, disadvantages, and limitations of each test method are presented.

GENERAL CONCEPTS

Biodegradability has now become a key word in the lexicon of those interested in the pollution problem. To many it means halting the spiraling mounds of garbage or developing a plastic bottle that will disintegrate. Why, suddenly, is everyone getting interested in biodegradability? Traditionally, nature provided the ultimate disposal of manmade waste, but as man advanced technologically, nature's work became more difficult. In fact, for some of the newer manmade substances, nature fails entirely to degrade them. Three examples that readily come to mind are plastic packaging materials, some of the detergents, and pesticides. Thus, the accumulation in the environment of many of the newer products synthesized by man has caused considerable interest to be focused on biological degradation, or biodegradability.

Biodegradability has been defined in several ways. Biodegradation can be the removal of organic matter from solution by enzymatic processes of oxidation and assimilation. Assimilation is the conversion of organic substances or substrates to new bacterial protoplasm. Certainly, the word "degrade" means to reduce the complexity of the substances. If we define biodegradation in terms of energy, then biodegradation consists of the consumption of a substance by biological action of living organisms with an accompanying degradation of energy. A layman's definition would be: An organic substance plus microorganisms yield carbon dioxide, water, and more organisms.

Note that in none of these definitions were the factors of time and extent mentioned. In the real world of wastewater treatment, the extent of biodegradation within a fixed time limit is a very important consideration to any working definition of biodegradability. Some researchers prefer not to use the term biodegradability in connection with wastewater treatment processes. They favor instead the term "treatability" in describing whether a substance is removed by biological waste treatment processes. The thinking is that the waste treatment processes place many constraints on the microorganisms that could prevent a compound from degrading. This argument is mostly from a scientific rather than practical point of view. Why are we mainly concerned about biodegradability? Aren't we really concerned about the nuisance value of a new substance and whether it is eliminated by treatment processes if it finds its way into the wastewater? In principle, laboratory testing should show the true biodegradability of the material tested as it would occur in the environment or in the waste treatment plants.

Obviously, most substances will ultimately be stabilized by microbial action, given enough time. We must then consider the biodegradation process as a rate process. For practical purposes of wastewater treatment, the substances should degrade at a rate equal to or less than the normal constituents of domestic waste after the bacteria have become acclimatized to the substances. In the activated sludge process, the time limit is 4 to 8 hr. In this definition, we are comparing one substance with another. The biodegradability of a material cannot be expressed as a single absolute figure, but as a relative figure because of the complexity of the biological degradation process. Attention should be directed to the fact that biodegradability is not a measurable property or condition of the water, but rather a property of the pollutant.

Although we usually think a compound has to be degradable to be removed by wastewater treatment, it is possible to remove the compound entirely by flocculation or adsorption. Toilet tissue may be considered in this category. Although it is slowly degraded by microorganisms, most of it is removed by sedimentation in the primary sedimentation tank, or by adsorption on the bacterial floc in the aeration tank. The activated sludge floc has great adsorption properties, and many organic substances are so adsorbed. In most cases it is true that a compound would be more environmentally acceptable if it were rapidly degraded by microorganisms.

How biodegradable should a compound be? The possibilities range all the way from slight to ultimate breakdown of the compound to cell matter, carbon dioxide, and water. Biodegradability must be measured in terms of its effect on the environment. In widespread use of a specific compound, a potential exists for significant environmental pollution if the compound is not degraded within a reasonable time in wastewater treatment plants or rivers. The future would indicate that the environmentally acceptable biodegradability criterion for products that become waterborne wastes should be that they are completely degraded to products that are harmless in surface and drinking waters.

TEST METHODS

Over the years, considerable research has been done on evaluating microbial breakdown by organic compounds. Techniques have ranged from Warburg respirometry used by microbiologists to BOD determinations and laboratory activated sludge units used by sanitary engineers.

The important feaures and limitations of various methods of testing biodegradability follow.

River Die-Away

The river die-away method is a very simple method and has been used by many investigators. The compound to be tested is added to a sample of river water and left at normal room temperature. Periodically, the solution is analyzed for the test compound to establish a die-away or disappearance curve. The curve usually shows a lag or no degradation for several days and then a rapid removal when the microorganisms have become acclimatized to the compound. The advantage of the river die-away test is that it requires very little equipment and it gives both the rate and the total degradability of the test material. The rate is only relaive; if, after the disappearance of the compound, an additional amount is added, it will disappear in less time. This can be repeated several times so that the die-away curve will have a sawtoothed appearance. Another modification that can be used to reduce the lag time and speed the process of acclimatization is to add a small amount of activated sludge to the river water.

The disadvantage of the test is that all rivers are not the same. Some have more microorganisms than others, and the pH and mineral constituents vary. To be able to use this procedure, it is necessary to be able to analyze for the compound. Likely, the method of assay will detect the original compound, but not a slight modification of the compound. Thus intermediate products could go undetected. In spite of the procedure's inherent drawbacks, it is useful in obtaining preliminary information on the ease of biodegradation. A large number of compounds can be screened in a relatively short time.

Warburg Respirometer

The disappearance of oxygen as the degradation proceeds is a general characteristic of aerobic biological systems. The Warburg respirometer is one of many apparatuses that permit oxygen uptake rates to be determined for a biological system. The reasons for its popularity are that it is commercially available, compact, and permits a number of samples to be run simultaneously.

There are a number of variables that can affect the results, but the most important factor is the nature and quantity of the microorganisms used. The seed used should be one that has become adapted to the test compound or that has at least been subjected to an adaptation period. As with any microbial growth system, the greater the initial number of microorganisms present, the more rapid the rate of oxygen utilization.

Advantages—

1. Direct measurement of biological oxidation is possible.
2. The method can be used for all compounds without using a different analytical test procedure. This is a decided advantage when no good analytical method exists.
3. Results are available within a reasonable time.
4. Oxygen consumption, radioactive carbon dioxide evaluation, and respiration assimilation balances can serve as bases for measuring biodegradability.
5. The method permits continuous observation of multiple samples over periods of a few hours or several days.
6. Lag periods and rate changes are readily determined.

Disadvantages—

1. Equipment is fairly expensive and requires a skilled technician.
2. The small sample size makes it difficult to obtain representative samples of sewage and some industrial wastes.
3. All organic matter added to the system is subject to oxidation, therefore necessitating pure organic compounds for fundamental studies.
4. With extended runs, nitrification can occur, giving high, erroneous results.
5. Oxygen uptake results are difficult to interpret quantitatively unless supplemented by other analyses.

Biochemical Oxygen Demand Test

The biochemical oxygen demand test (BOD) is one of the older methods of evaluating the biodegradability of substances. It was first published as a standard by the Royal Commission for Sewage Disposal in 1912. For many years, nothing better was available for determining the strength and controlling the treatment of wastewater. In the BOD test, the amount of dissolved oxygen utilized during 5 days when the sample is stored in a filled bottle in the dark at 20 C is measured. Instead of a single determination, a curve of oxygen uptake as a function of time can be developed if a series of duplicates are run. With the development of reliable oxygen-sensing probes, it is now possible to determine the oxygen content at intervals or continuously over the entire test period. Another modification of the testing apparatus is that the oxygen uptake and BOD are determined electronically from the electrical current consumption needed to generate the oxygen required to maintain the pressure equilibrium in the flask.

The BOD test has numerous limitations when test results are used to predict what will take place in a waste treatment plant or in a stream. Only those limitations pertinent to utilization of the method for determining biodegradability will be discussed.

Advantages—

1. The apparatus and testing procedure are very simple. The test does not require a highly trained technician.
2. A large amount of BOD data are available on compounds with known waste treatability in our present waste treatment systems.
3. The small number of bacterial cells used and the food free BOD dilution water minimizes interferences with chemical analyses either for the parent compound or intermediate breakdown products.
4. Carbon dioxide is present throughout the test period and does not become limiting as is possible in the Warburg procedure. It has been reported that complete absence of carbon dioxide inhibits assimilation of organic matter by bacteria.

5. Problems of aeration and oxygen transfer are not encountered because all the oxygen required is present at the beginning of the test.

Disadvantages—

1. The amount of sample that can be used is small because of the limited solubility of oxygen in water.
2. The testing period is long, although some indication can be obtained in less time if the oxygen uptake is measured periodically.
3. As with the Warburg procedure, nitrification and extraneous organic matter can lead to erroneous conclusions.
4. The interpretation of results has the same limitations as the other types of respirometer methods in that results are not direct convertible to percentage of the compound degraded.

Flask Test Method

The flask test method is the most widely used technique of all the laboratory procedures except for activated sludge. There are many versions of the test procedure, but most use a preadapted seed and a chemically defined medium. The flasks may be aerated by continuous shaking on a mechanical shaker, agitated with magnetic stirrers, aerated through a ceramic filter, stirred with a paddle stirrer, or merely left quiescent. The test mixture can be analyzed each day or at the end of the specified time period. If degradation is not evident or toxicity is evident, the test compound should be run at a lower concentration. Parallel runs with known degradable compounds are advisable to insure that the test conditions were correct. It is suggested that a compound of similar structure and class serve as a reference standard.

The popularity of the flask test method is exemplified by the fact that five leading countries have adopted some version of the method as their screening or presumptive test method for determining the biodegradability of anionic detergents.

Advantages—

1. The flask test method does not require elaborate or specialized laboratory equipment.
2. Reproducibility is generally good.
3. Sample size is not limited.
4. The test compound does not have to be pure.
5. Metabolic products can be studied without too much interference if mineral salts are used and the test compound is the sole carbon source.

Disadvantages—

1. The flask test method does not show the time required for adaptation since an adapted culture is used.

2. A separate adapting process is required if adaptation is not made a part of the test procedure.

3. Shaking on a mechanical shaker limits the amount of sample that can be run.

4. No waste treatment process is simulated.

5. A chemical or physical analytical test method must be available for each class of compounds tested or a material balance must be run.

6. Simple analytical procedures do not generally measure degradation residues.

Activated Sludge Method

The activated sludge process is one of the most important wastewater treatment processes. Laboratory scale models of the process have been used for many years to study the treatability of various industrial wastes. It was natural that the method should become a major tool in biodegradability testing.

The laboratory methods based on the activated sludge principle vary in feed, residence time, and type of run (continuous or batch-fed). The continuous activated sludge system is preferred because it corresponds more nearly to practical conditions. A system that approximates the operation of a plug flow aeration tank was developed by Butterfield back in 1937. It is known as the fill-and-draw or the semicontinuous process. In this method of testing, the bacteria inoculum, the test material, and the feed are placed in an aerated vessel. The feed is usually a chemically defined medium. The mixture is aerated for a period of time, usually 23 hours. Then the air supply is turned off and the mixture allowed to settle. A portion of the supernatant is removed and replaced with new feed containing the test compound. This procedure is then repeated for the duration of the test. If the test period is long, it is necessary to periodically waste some activated sludge to maintain a reasonable level of bacteria. In all aerobic biological processes there is a net increase in bacterial cells.

Although each cycle in the semicontinuous operation constitutes a batch run, the method closely approaches plug flow conditions in a conventional activated sludge plant. The aeration basin of the activated sludge process is usually long and narrow. The recycle sludge and the wastewater enter at one end of the aeration tank. Ideally, the mixture moves as a plug the entire length of the tank. The bacteria are subjected to all phases of the bacterial growth curve, from the log phase to the endogenous stage. That is, at the head end of the tank, the bacteria have an ample supply of food upon which to feed. In this portion of the tank the bacteria are growing most rapidly, and consequently the removal rate of the organic matter is the greatest here. As the plug moves along the tank, the food becomes depleted, and if the retention in the basin is correct, the bacteria will start to enter the endogenous phase just as the plug reaches the end of the aeration basin.

The laboratory activated sludge units used by investigators have varied in capacity from a few hundred milliliters to several gallons, depending on the nature of the study. The volume should not be too small or sampling would disturb the system. For biodegradability testing it is not necessary to maintain a large unit. Small units are much more desirable because of space, cost, and labor of servicing several large units. On scaling down to very small units, there is some difficulty in designing settling chambers. In most units the settling chambers are an integral part of the aeration tank rather than separate units. The majority of the laboratory units are of the completely mixed type rather than plug flow.

Advantages—

1. The continuous and the semicontinuous methods simulate in the laboratory the treatment that wastewater normally receives.
2. There is an accumulation of knowledge over the years since the method has been used.
3. Reproducibility is very good if the unit is operated until steady state is achieved.
4. Sample size is not limited.
5. The test compound does not have to be pure.

Disadvantages—

1. Continuous operating units require money, space, and maintenance.
2. Single batch runs do not allow for acclimatization unless the test period is unduly prolonged.
3. Residence time of 23 hr in the fill-and-draw method is not typical of treatment plants and is not therefore realistic.
4. Most investigators feel that valid results cannot be obtained in less than 10 days. There are always unexplainable fluctuations in the efficiency of the process that must be averaged.
5. A chemical or physical analytical method must be available for the analysis of each compound if wastewater is used as feed. If mineral salts medium is used, BOD or COD tests can be used to calculate a material balance.

FUTURE REQUIREMENTS OF BIODEGRADABILITY

The emphasis on biodegradable materials that emerged around 1960 relative to detergents may be expected to continue. In fact, the requirements for biodegradable compounds will increase as the world becomes more conscious of pollution in its waterways. In the United States, there is no Federal law or regulation requiring that compounds be biodegradable. Several local ordinances have been passed restricting the sale and use of biologically nondegradable detergents.

In the future, products that will become a constituent of wastewater will not receive serious consideration for big markets if they are not fully biodegradable.

In general, there is still lack of agreement on a standard test procedure. In fact, there is no satisfactory definition of the term biodegradable that is acceptable to all. The question concerning the biological degradability of a compound can only be answered by a biological test. The structure of a compound can be of assistance in predicting the behavior of the compound, but biodegradability depends on many factors, such as size of the molecule, solubility, and surface activity. Predictions are more reliable when dealing with a homologous series than when making gross comparisons based on functional groups or straight chains.

In determining the treatability of waste, the rate and the extent of degradation must be considered. The rate at which a certain property of a substance changes as a function of time elapsed is not difficult to determine. It is the extent of degradability that poses the problem. There is a need to know if any degradation products are formed in the process as intermediate or end products. The metabolic products, like other nonbiodegradable pollutants, can build up in the surface water supplies, making them undesirable for reuse, or they can build up in food chains, causing damage to aquatic life.

RENOVATED WATER FROM MUNICIPAL SEWAGE TREATMENT PLANTS

Apolinary L. Kowal

ABSTRACT

Renovation of secondary effluent from a trickling filter and an activated sludge plant were investigated. Coagulation, sedimentation, recarbonation, filtration, and sorption were applied.

The investigation was performed on both laboratory and pilot scale. Inflow to the sewage treatment plants was characteristic of municipal sewage. BOD of the inflow ranged from 121 to 360 g/m^3 O_2, *average treatment efficiency of the trickling filter and activated sludge plant was 86% removal of BOD, and 37% and 84% removal of ammonia nitrogen, respectively. Ammonia nitrogen concentration in the secondary effluent from the activated sludge plant was relatively low (up to 6.1* g/m^3 *N), and very high in the secondary effluent from the trickling filter plant (up to 26* g/m^3 *N. Jar test coagulation of the secondary effluent required high doses of the coagulants. The coagulant doses were lower when the process was performed in the sludge blanket clarifier. Lime was established as the most economical coagulant. Application of iron and alum salts resulted in an increase of sulphate, whereas large doses of lime increased hardness and alkalinity of the water, so that the recarbonation followed by sedimentation was obligatory. The best removal of hardness and alkalinity was acquired through a recarbonation after coagulation and sedimentation. An optimum dose of lime to coagulate the activated sludge plant secondary effluent fluctuated from 200 to 1200* g/m^3 *CaO. The higher the concentration of phosphate and the higher the permanganate values of treated water, the higher the doses of lime that were required.*

The use of flocculants of domestic production (Rokrysol WF-1 nonionic, WF-2 anionic, WF-3 cationic) improved the effect of coagulation slightly and mainly aided flocculation and sedimentation. Sorption on a carbon slurry in simultaneous coagulation and sorption, or sorption on a carbon filter bed following coagulation, decreased the permanganate value about 30% compared with single coagulation. Removal of ammonia nitrogen in all investigated processes was insignificant. The permanganate value of the renovated water could be lowered up to 5.2 g/m^3 O_2, *and phosphate concentration to 0.07* g/m^3 *P. The color and turbidity of renovated water were close to drinking water standards.*

INTRODUCTION

Water renovation of secondary effluent from sewage treatment plants in Walbrzych (trickling filters and an activated sludge plant) were investigated. Lime, iron and alum coagulation, sedimentation, recarbonation, filtration, and sorption were employed. Effectiveness of COD, BOD, phosphate, and turbidity removal was high. Removal of nitrogen ammonia was insufficient.

About 75% of water demanded by municipalities and industries in Poland is supplied from surface water sources. In the year 1990, this proportion will rise to about 85%. The water demand will approach 30 billion m^3, an amount equal to the entire discharge of the rivers in a dry year. By the year 1990, with increased industrialization, agricultural production, and demand for water by the population, much of the surface water can be expected to be so affected by pollution that present methods of sewage treatment may not produce the required degree of purity. The increase in biogenic and refractory substances in surface waters already limits the possibilities of some waters being utilized for municipal and also for industrial supply. Protection against pollution and improved water quality will require the application of tertiary treatment of sewage and water renovation processes.

In many cases, the quality of renovated water is better than water from polluted rivers. Sanitary, hygienic, and aesthetic considerations and also the increased concentration of refractory and mineral substances prevent the use of renovated waters for direct municipal supply without self-purification in a receiving stream.

By using renovated water for industrial supply, the self-purification process may be bypassed and waters of drinking quality will be conserved. This approach has particular significance for regions experiencing water shortage. The Institute of Environmental Protection Engineering of the Wroclaw Technical University undertook research on the renovation of secondary effluent from the Walbrzych sewage treatment plants. In 1973 they used biological filters, and in 1975, an activated sludge plant.

The sewage reaching the plants is predominantly from residential areas with a small proportion of sewage from food industries. The characteristics of influent and secondary effluent are given in Tables 1 and 2.

EFFECT OF WATER RENOVATION PROCESSES ON SECONDARY EFFLUENT FROM A TRICKLING FILTER PLANT

The investigation of water renovation from the biological filter effluent was performed on a laboratory and a pilot scale. The inflow to the trickling filter plant in Walbrzych is characteristic of municipal sewage. The pH ranged from 7.4 to 7.9, and the alka-

TABLE 1. CHARACTERISTICS OF INFLUENT AND SECONDARY EFFLUENT FROM A SEWAGE TREATMENT PLANT (BIOLOGICAL FILTERS) IN WALBRZYCH

	Influent			Secondary effluent		
Characteristic	Min	Max	Mean	Min	Max	Mean
pH	7.4	7.9	7.7	7.4	8.1	7.6
Alkalinity, g/m^3 $CaCO_3$	280	330	305	165	290	230
Permanganate value, g/m^3 O_2	33	180	83	8	32	18.4
BOD, g/m^3 O_2	121	360	237	14	58	33
COD, g/m^3 O_2	......	......	......	......	......	......
Ammonia, g/m^3 N	32	54	39	12	44	26
Orthophosphate, g/m^3 N	3.8	5.9	4.6	0.7	4.0	2.9
Dissolved solids, g/m^3	438	619	529	368	536	475
Suspended solids, g/m^3	62	270	187	2	152	69

TABLE 2. CHARACTERISTICS OF INFLUENT AND SECONDARY EFFLUENT FROM A SEWAGE TREATMENT PLANT IN WALBRZYCH (ACTIVATED SLUDGE)

	Influent			Secondary effluent		
Characteristic	Min	Max	Mean	Min	Max	Mean
pH	6.5	9.1	7.4	6.2	7.8	7.2
Alkalinity, g/m^3 $CaCO_3$	140	375	295	55	225	130
Hardness, g/m^3 $CaCO_3$	215	645	290	210	320	245
Permanganate value, g/m^3 O_2	64.0	250.0	143.0	4.5	173.0	21.6
BOD, g/m^3 O_2	134	640	312	8.5	285	43.4
COD, g/m_3 O_2	121	519	315	41	83	56.2
Ammonia, g/m^3 N	17.6	93.0	39.5	0.4	18.6	6.1
Total phosphorus, g/m_3 P	1.7	13.0	7.7	3.2	7.3	5.3
Orthophosphate, g/m^3 P	9.9	13.7	5.5	0.7	11.7	4.0
Dissolved solids, g/m^3	266	916	649	364	791	559
Suspended solids, g/m^3	84	11.9	433	6	152	68

linity ranged from 280 to 330 g/m^3. The permanganate value stayed within wide limits, from 33 to 180 g/m^3 O_2, and the BOD ranged from 121 to 360 g/m^3 O_2. The average ammonia nitrogen concentration was 39 g/m^3 N, and the phosphates were 14.0 g/m^3 PO_4^{-3}. The efficiency of treatment was sufficient to obtain 77.8% reduction for the permanganate value, 86.1% for the BOD, 33% for the ammonia nitrogen, and 37.1% for the phosphate. (Table 1).

In the laboratory tests, the secondary effluent coagulated with lime or aluminum sulphate was subjected to sedimentation and then to filtration on a sand bed and through the activated carbon (Carbon Z-4) filters. When lime was used, the sewage before filtration was recarbonated with carbon dioxide and again allowed to settle. The best results in these tests were achieved by a dose of 1000 g/m^3 $Al_3(SO^4)_3 \cdot 18H_2O$, which induced reduction of (a) color intensity from 120 g/m^3 Pt to 20 g/m^3 Pt, (b) permanganate value from 40 to 9 g/m^3 O_2, and (c) BOD from 140 to 8.8 g/m^3 O_2. Turbidity was completely removed (Table 3). The use of a dose amounting to 1600 g/m^3 CaO decreased the color to 10 g/m^3 Pt and the permanganate value to 13 g/m^3 O_2. The sewage pH was about 8.3, alkalinity was 200 g/m^3, and hardness was 255 g/m^3 (Table 4). The best treatment results in laboratory tests employed a simultaneous coagulation with a carbon slurry (Carbopol Z-4).

TABLE 3. EFFECT OF ALUM COAGULATION ($1000\ g/m^3\ Al_2(SO_4)_3 \cdot 18\ H_2O$) OF SECONDARY EFFLUENT

Treatment phase	Color, g/m^3 Pt	Turbidity, g/m^3 SiO_2	pH	BOD, g/m^3 O_2	Permanganate value g/m^3 O_2	Permanganate value % Removal
Secondary effluent	120	50	8.6	140	40	
Coagulation	30	0	6.2	9.6	16.2	60
Filtration	20	0	6.2	......	17	57
Carbon sorption	20	0	6.7	8.8	9.0	77

TABLE 4. EFFECT OF LIME COAGULATION ($1600\ g/m^3$ CaO) OF SECONDARY EFFLUENT

Treatment phase	Color, g/m^3 Pt	Turbidity, g/m^3 SiO_2	pH	Alkalinity, g/m^3 $CaCO_3$	Hardness, g/m^3 $CaCO_3$	BOD, g/m^3 O_2	Permanganate value g/m^3 O_2	Permanganate value Removal %
Secondary effluent	120	50	8.6	265	250	140	40	....
Coagulation	30	10	12.5	1320	1320	......	13.2	67
Recarbonation	20	0	8.3	200	315	10.0	14.0	65
Filtration	20	0	8.3	200	315	8.0	13.0	67
Carbon sorption	10	0	8.3	200	255	......	13.0	67

Simultaneous coagulation with an optimum dose of 1000 g/m^3 $Al_2(SO_4)_3 \cdot 18H_2O$ and 800 g/m^3 powdered carbon decreased the permanganate value from 50 to 4.8 g/m^3 O_2 (Table 5) and completely removed turbidity (Table 6).

In the pilot plant investigations, the secondary effluent was coagulated with the aluminum sulphate or with lime in a clarifier

TABLE 5. ALUM COAGULATION (1000 g/m^3 Al$_2$ (SO$_4$)$_3$·18H$_2$O) AND CARBON SORPTION OF SECONDARY EFFLUENT*

Carbon dosage, g/m^3	Color, g/m^3 Pt	pH	Permanganate value g/m^3 O$_2$	Permanganate value % Removal
Secondary effluent	100	8.2	50	......
0	30	5.6	16.2	68
50	15	5.4	12.2	76
100	10	5.5	12.2	76
200	5	5.5	7.8	84
400	0	5.6	6.0	88
800	0	5.6	4.8	90

* Turbidity was reduced to zero by this treatment.

TABLE 6. LIME COAGULATION (800 g/m^3 CaO) AND CARBON SORPTION OF SECONDARY EFFLUENT

Carbon dosage, g/m^3	Color, g/m^3 Pt	Turbidity, g/m^3	pH	Alkalinity, g/m^3 CaCO$_3$	Permanganate value g/m^3 O$_2$	Permanganate value % Removal
Secondary effluent	30	50	8.0	230	24.4	......
0	20	0	12.4	490	9.8	61
100	10	0	12.4	350	7.8	72
200	5	0	12.4	340	5.6	78
400	3	0	12.4	280	5.6	78
800	3	0	12.4	280	5.6	78

with sludge blanket and then filtered through double media filters composed of sand-anthracite and of sand-carbon. The output of the system ranged from 5 × 10^{-2}m^3/hr in coagulation with aluminum sulphate, and 1 × 10^{-3}m^3/hr in coagulation with lime. The filtration velocity was 5 m/hr. The tests were executed in two series. The cycle with one dose of coagulant came to 3 days. Results were given as an average of the two series of measurements. With a dose of aluminum sulphate amounting to 120 g/m^3 Al$_2$ (SO$_4$)$_3$ · 18H$_2$O, the color decreased from 50 to 12 g/m^3 Pt, the permanganate value from 26.5 to 8.7 g/m^3 O$_2$, and the turbidity from 30 to 6 g/m^3 SiO$_2$ (Table 7). The ammonia nitrogen was not significantly removed. A dose of 600 g/m^3 CaO decreased the color from 50 to 13.3 g/m^3 Pt when filtered on the sand-anthracite bed, and further reduced it to 4.0 g/m^3 Pt when filtered on a sand-carbon bed. The permanganate value was decreased from 27.1 to 8.7 and to 6.5 g/m^3 O$_2$, respectively. The hardness of the sewage was very high, up to 1305 g/m^3 (Table 7).

TABLE 7. EFFECTIVENESS OF COAGULATION, SORPTION, AND FILTRATION OF SECONDARY EFFLUENT IN PILOT PLANT

Treatment phase	Coagulant	Dosage, g/m³	Color, g/m³ Pt	Turbidity, g/m³ SiO_2	Hardness, g/m³ $CaCO_3$	Permanganate value		Ammonia, g/m³ N
						g/m³ O_2	% Removal	
Secondary effluent	......	60	22	8	......	26.0	......	27.6
Coagulation	$Al_2(SO_4)_3 \cdot 18H_2O$	......	11	8	......	18.0	28.1	21.0
Filtration	......	......	5	3	......	11.5	54.0	13.6
Secondary effluent	......	......	50	30	......	26.5	......	40.1
Coagulation	$Al_2(SO_4)_3 \cdot 18H_2O$	120	40	24	......	15.5	49.1	35.7
Filtration	......	......	12	6	......	8.7	67.0	27.1
Secondary effluent	......	......	25	8	......	36.0	......	13.7
Coagulation	$Al_2(SO_4)_3 \cdot 18H_2O$	200	10	4	......	25.0	31.2	22.0
Filtration	......	......	9	3	......	17.5	51.5	15.2
Secondary effluent	......	......	47.5	44.3	225	38.3	......	57.3
Coagulation	CaO	200	33.5	27.7	260	21.4	34.3	53.6
Filtration	......	......	22.7	14.7	230	17.5	50.9	48.5
Sorption	......	......	26.0	14.0	225	12.3	68.1	52.0
Secondary effluent	......	......	50.05	50.0	230	45.0	......	98.0
Coagulation	CaO	400	27.0	28.0	335	18.7	58.4	80.0
Filtration	......	......	21.0	8.0	295	18.6	58.4	74.0
Sorption	......	......	19.0	8.0	285	18.3	68.3	82.0
Secondary effluent	......	......	50.0	50.0	220	27.1	......	66.6
Coagulation	CaO	600	13.3	10.0	1305	8.5	69.0	56.0
Filtration	......	......	13.3	3.0	1290	8.7	68.0	54.8
Sorption	......	......	4.0	3.4	1290	6.5	76.0	55.2

EFFECT OF WATER RENOVATION PROCESSES ON SECONDARY EFFLUENT FROM AN ACTIVATED SLUDGE PLANT

The sewage treatment plant is newly constructed. Incoming sewage is comminuted, treated in sand traps, primary sedimentation tanks, and activated sludge tanks with a high-rate aeration system, and finally settled. Average flow fluctuated during the study from 502 to 1148 m^3/hr. The average permanganate value of the sewage was 143 g/m^3 O_2. The efficiency of sewage treatment was 84.9% reduction of permanganate value, 86.1% of BOD, and 82.1% of COD (Table 2). The effects of coagulation on the secondary effluent with ferric sulphate, aluminum sulphate, and lime were determined in laboratory tests performed in 1975. The sewage, after jar test coagulation, was settled for 1 hr, and the supernatant was decanted and analyzed. The optimum dose of lime ranged from 200 to 1200 g/m^3 CaO. The coagulation of secondary effluent with a dose of 1200 g/m^3 CaO decreased the permanganate value from 34 to 18.4 g/m^3 O_2 and removed the phosphate and turbidity. High concentrations of phosphates or high permanganate value of the secondary effluent required high doses of lime, up to 1200 g/m^3 CaO; whereas with low permanganate values and low concentrations of phosphates, the dose was close to 200 g/m^3 CaO. The average and the extreme concentrations of the characteristics of the renovated water are given in Table 8. Use of the flocculants Rokrysol WF-1 (nonionic polyelectrolyte), Rokrysol WF-2 (anionic), and Rokrysol WF-3 (cationic) only slightly improved the effects, aiding only flocculation. All the samples coagulated with flocculants had a high opalescence. The recarbonation of water coagulated with lime was achieved with the use of carbon dioxide in the following variants:

TABLE 8. CHARACTERISTICS OF SECONDARY EFFLUENT BEFORE AND AFTER LIME COAGULATION

		Secondary effluent			CaO Coagulation		
Characteristic	Unit	Min	Max	Mean	Min	Max	Mean
pH	......	8.2	8.6	8.3	11.0	12.5	11.6
Permanganate value	g/m^3 O_2	11.2	34.0	18.9	5.1	18.4	8.8
Orthophosphate	g/m^3 P	0.91	5.2	2.54	0.00	0.13	0.06
Color	g/m^3 Pt	8	50	35.7	0	25	14
Turbidity	g/m^3	5	30	18.7	0	0	0

A. The carbon dioxide was brought to the water and coagulated with lime after 3 min of rapid mixing. Then after the pH reached 8.3, the water was mixed slowly for 20 min, settled for 1 hr, and decanted.

B. The process of recarbonation was carried out simultaneously with dosing the lime, thus maintaining a constant pH of 9.

C. After coagulation and sedimentation, the water was recarbonated, settled, and then again decanted.

D. After the coagulation and decantation, 15 g/m^3 of Rokrysol WF-1 was added to the sample; following this, it was recarbonated and sedimented, as in test C.

The best hardness and alkalinity removal were acquired through recarbonation after coagulation and sedimentation. The hardness of water after recarbonation was lower than the hardness of secondary effluent. A raised permanganate value was ascertained in all samples of recarbonated water. The concentration of phosphates decreased only in Willow Method C. The turbidity of water from precipitation of fine crystalline calcium carbonate was higher in all samples than the turbidity in a coagulated sample alone (Table 9). Coagulation with a dose of 400 g/m^3 $Al_2(SO_4)_3 \cdot 18H_2O$ at a variable pH (from 5.9 to 7.8) decreased the permanganate value from 16.0 to about 7 g/m^3 O_2. The best results were achieved using a pH of 6.3 to 7.0. Phosphates were removed by 97%, and the removal level was independent of the water pH. Turbidity was removed completely. Concentration of residual aluminum fluctuated from 0.05 to 1.8 g/m^3 Al. Average and extreme values for secondary effluent characteristics coagulated with the optimum doses of ferric or aluminum sulphate are listed in Table 10. The optimum sulphate dose of 400 g/m^3 $Al_2(SO_4)_3 \cdot 18H_2O$ reduced the permanganate value from 37% to 72%, phosphates by more than 98%, and color from 38% to 49%. Turbidity was completely removed. Average concentration of aluminum in samples coagulated with the optimum dose was 0.65 g/m^3 Al (Table 10). The use of the polyelectrolytes Rokrysol WF-1, WF-2, WF-3, and Gigtar with

TABLE 9. EFFECT OF LIME COAGULATION AND RECARBONATION ON SECONDARY EFFLUENT

Characteristic	Unit	Secondary effluent	Lime coagulation alone	Recarbonation (1200 g/m^3 CaO) method			
				A	B	C	D
pH	......	7.4	12.5	8.3	8.9	8.3	8.4
Permanganate value	g/m^3 O_2	18	8.8	12.8	12.0	10.8	11.6
Orthophosphate	g/m^3 P	8.9	0.2	0.2	0.78	0.00	0.20
Color	g/m^3 Pt	28	15	25	25	16	15
Turbidity	g/m^3	30	0	15	20	30	30
Ammonia	g/m^3 N	11.6	10.9	11.6	9.5	10.5	9.8
Alkalinity	g/m^3 $CaCO_3$	150	1500	280	250	180	200
Hardness	g/m^3 $CaCO_3$	2050	2070	340	255	190	195

TABLE 10. CHARACTERISTICS OF SECONDARY EFFLUENT BEFORE AND AFTER IRON AND ALUM SALTS COAGULATION

Characteristic	Unit	Secondary effluent			Coagulant with $Fe_2(SO_4)_3 \cdot 9H_2O$			Coagulant with $Al_2(SO_4)_3 \cdot 18H_2O$		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
pH	pH	7.2	8.3	7.8	6.8	7.7	7.2	6.9	7.7	7.6
Permanganate value	g/m^3 O_2	14.2	23.2	17.3	4.3	8.2	6.1	4.8	9.0	6.8
Orthophosphate	g/m^3 P	2.5	3.3	2.9	0.03	0.06	0.03	0.03	0.09	0.05
Color	g/m^3 Pt	16	35	27	5	26	15	5	18	12
Turbidity	g/m^3	20	30	28	0	0	0	0	0	0
Aluminum	g/m^3 Al	0.0	0.3	0.06	......	......	......	0.05	1.8	0.65
Iron	g/m^3 Fe	0.2	0.89	0.29	0.31	0.89	0.50	......	......	......

100 g/m^3 $Al_2(SO_4)_3 \cdot 18\ H_2O$ did not improve the effectiveness of the process, whereas the concentration of aluminum increased slightly. Coagulation with 100 g/m^3 $Fe_2(SO_4)_3 \cdot 9H_2O$ and with pH 2.9 to 7.4 induced a decrease in permanganate value from 44% to 55%, and in phosphates from 94% to 96% (i.e., from 0.2 to 0.3 g/m^3 PO_4^{-3}). The lowest concentration of iron was attained by a pH higher than 7.4. Coagulation with an optimum dose of ferric sulphate amounting to 200 g/m^3 $Fe_2(SO_4)_3 \cdot 9H_2O$ decreased the permanganate value from 42% to 78% and the phosphates by more than 98%. Turbidity was totally removed. The concentration of iron in samples did not exceed 0.89 g/m^3 Fe. The use of the polyelectrolytes Rokrysol WF-1, WF-2, WF-3, and Gigtar induced an insignificant improvement in the level of permanganate removal. Large doses of cationic WF-3 affected the removal of phosphates and iron in the coagulated water.

DISCUSSION

The coagulation of secondary effluent from biological filters required high doses of coagulants and high doses of powdered activated carbon as a result of a high concentration of dissolved organic compounds biologically undegradable. The proportion of the permanganate value to BOD of secondary effluent during the tests was about 0.73. The employment of a clarifier with sludge blanket increased the contact with a precipitated coagulant and gave good results in treatment efficiency, with doses of coagulants lower than in the jar tests. An optimum dose of lime used to coagulate the secondary effluent from the activated sludge plant fluctuated from 200 to 1200 g/m^3 CaO. In the water with a high permanganate value or with high concentration of phosphates, the dose approached 1200 g/m^3 CaO. The use of higher lime doses allowed the removal of phosphates; the permanganate value however was relatively high. High doses of lime increased the hardness and alkalinity of the water. Recarbonation decreased hardness, alkalinity, and pH. Increased turbidity was caused by a fine-grained crystalline calcium carbonate. Coagulation of the latter with a freshly precipitated sediment decreases pollutant removal.

A simultaneous coagulation and recarbonation did not improve the effect of treatment. Changes in the sewage reactions from pH 5.9 to 7.8 in coagulation with aluminum sulphate, and from pH 2.9 to 7.4 in coagulation with ferric sulphate had no clear influence on the effects of pollutant removal, with the exception of the color. Lowering the phosphate concentration to below 0.2 g/m^3 PO_4^{-3} required a fourfold excess of aluminum or iron ions in proportion to the initial concentration of the phosphates. The use of ferric or aluminum sulphate for coagulation resulted in an increased concentration of dissolved solids.

WASTEWATER REUSE PRACTICE IN THE UNITED STATES

Carl A. Brunner

ABSTRACT

Wastewater reuse in the United States is presently being practiced for agricultural, industrial, and recreational purposes. One example of nonpotable domestic reuse exists, but at this time there are no examples of potable domestic reuse. As of 1971, the volume of water reused was 133 billion gal per year. Nearly 58% of this volume was used for irrigation. Most of the remainder was used for cooling water.

BACKGROUND

Sound management of water resources must include consideration of the potential reuse of properly treated municipal wastewater as an alternative for meeting future water demands. Though the need for additional water supplies is greatest in the arid Southwest, some areas in the eastern part of the United States are also observing water shortages. Groundwater in many places is being mined or used faster than it is being replaced by natural means. In groundwater-using areas such as Southern California and Long Island, alternative methods of obtaining water are very expensive. Where the cost of new water sources is high or where legal constraints are placed on new sources, wastewater reuse may be an attractive alternative. The potential benefits of wastewater reuse were recognized in Public Law 92-500, the Federal Water Pollution Control Act Amendments of 1972, and more recently in the Safe Drinking Water Act of 1974. There is a clear national mandate to conserve our water resources by renovating and reusing wastewater.

Possible wastewater reuse applications include irrigation and other agricultural uses; industrial uses such as cooling water, process water, and boiler feed water; use in recreational lakes; use for fish propagation; and use for nonpotable and potable domestic purposes. All but potable reuse are practiced in the United States, although use for fish propagation is very limited. The degree of sophistication of wastewater treatment varies with the reuse application from conventional secondary treatment (or in some cases primary treatment) to rather elaborate advanced systems.

The following information is derived largely from a survey of reuse made for the Environmental Protection Agency (EPA) by Schmidt and Clements (Schmidt, C. J., Clements, E. V., "Demonstrated Technology and Research Needs for Reuse of Municipal Wastewater," EPA-670/2-75-038, May 1975.) Data were collected during the period 1971-73.

IRRIGATION

According to the EPA survey, of the 133 billion gal water reused in 1971, 77 billion gal, or 58%, was for agricultural purposes. Practically all of the 77 billion gal was for irrigation. The number of plants utilizing their wastewater for irrigation at that time was 337, but 205 of these were on a very small scale. Irrigation applications included agricultural crops, pasture land, turf, and landscape.

The type of treatment given to municipal wastewater before utilization for irrigation varies from primary to tertiary. Table 1 shows the distribution of treatment methods. For many crops, primary treatment is all that is necessary. The majority of plants do, however, provide secondary treatment.

TABLE 1. MUNICIPAL TREATMENT PROVIDED FOR IRRIGATION REUSE ON SPECIFIC CROPS

Crop	Number of treatment plants*	Treatment level (% of plants)		
		Primary	Secondary	Tertiary
Grain	17	23	77	0
Corn	11	36	64	0
Vegetables	6	14	86	0
Fruit	12	18	82	0
Cotton	26	29	71	0
Fodder	51	24	73	3
Pasture	34	20	71	9
Turf and landscape	47	9	70	21

* Certain plants supply water to more than one crop.

Distance from treatment plant to point of reuse is an important economic consideration. In the case of irrigation, 1971 results indicated that 20% of the users were located adjacent to the treatment plant, and fewer than 6% were more than 4 mi away.

Wastewater is made available for irrigation primarily as a means of disposal, not for economic gain. Only a small percentage of producers charge users, and these charges are generally much less than the cost of treatment. Any payment is, however, to the benefit of the municipality, assuming the irrigation use does not increase the degree of treatment provided.

INDUSTRIAL REUSE

The EPA survey indicated that industrial reuse amounted to 53.5 billion gal/year, or 40% of the total water reused. One user, Bethlehem Steel in Baltimore, Maryland, accounted for 44 billion gal/year. There were a total of 15 treatment plants producing water for industrial reuse. The total volume for this reuse application will increase substantially since at least one renovation plant is presently being constructed, that at Contra Costa, California.

Utilization for cooling water represents by far the largest industrial reuse—more than 98%. Of the 15 industrial reuse facilities, 12 are primarily for cooling.

The degree of treatment needed for cooling water depends on whether the cooling system is once through or recirculating. For once through systems, high quality secondary treatment is a minimum requirement. Table 2 shows the type of treatment required in five recirculating systems.

TABLE 2. EFFLUENT QUALITY VERSUS USER TREATMENT REQUIRED FOR COOLING TOWER MAKEUP WATER

	Effluent quality, mg/l			User treatment
Selected users	BOD	SS	TDS	processes
City of Burbank, California	2	2	500	Shock chlorination, pH adjustment, corrosion inhibitor
Nevada Power Co., Las Vegas, Nevada	20	20	1,000-1,500	Shock chlorination, lime clarification, pH adjustment, corrosion inhibitor
Southwestern Public Service Company, Amarillo, Texas	10	15	1,400	Lime clarification, pH adjustment, shock chlorination, corrosion inhibitor
City of Denton, Texas	30	30	130	Shock chlorination, pH adjustment, corrosion inhibitor (treatment insufficient for effluent of this quality)
El Paso Products Co., Odessa, Texas	10	13	1,300	Lime clarification, pH adjustment, filtration, softening

Three industrial plants utilize wastewater for boiler water makeup. Each user provides substantial additional treatment, as shown in Table 3.

TABLE 3. COMPARISON OF TREATMENT PROCESSES UTILIZED FOR PRODUCING BOILER FEED MAKEUP WATER FROM MUNICIPAL SEWAGE EFFLUENT

Company and boiler pressure	Treatment processes	Product water quality, ppm as $CaCO_3$
Cosden Oil & Chemical Co., Big Spring, Texas (175 psig boilers)	Hot process lime clarification, anthracite filtration, hot zeolite softening, and deaeration.	TDS, 443; hardness, 0-2
El Paso Products Co., Odessa, Texas (200 psig boilers)	Cold lime clarification, recarbonation, anthracite, filtration, zeolite softening, and deaeration.	TDS, 1,000; hardness, 0-2
El Paso Products Co., Odessa, Texas (650 psig boilers)	All of above for low pressure boilers plus demineralization through cation and anion exchangers.	TDS, 0-2; hardness, 0
Southwestern Public Service Co., Lubbock, Texas (1,500 psig boilers)	Cold lime clarification, pH adjustment, reverse osmosis, followed by demineralization with cation and anion exchangers, and a mixed bed exchanger for final polishing.	TDS, 0-1; hardness, 0

Three plants reported using wastewater for processing purposes. All were in the mining and steelmaking industries and did not require particularly high quality water.

In most cases of industrial reuse, this source is used because it is cheaper than alternative sources. As in the case of irrigation reuse, municipalities selling the water charge only a small fraction of the cost of treatment. The highest value reported was 14.4¢/1000 gal. In none of the 15 cases, however, do the municipalities provide treatment beyond that required for surface discharges. Substantial additional treatment is provided by the user in some cases (see Table 3). For cooling water, these additional treatment costs vary from 10¢/1000 gal to 55¢/1000 gal. One reported cost for boiler water makeup was 74¢/1000 gal.

RECREATIONAL REUSE

The use of properly treated municipal wastewater to create recreational lakes has been carried out in at least three instances in the State of California. The oldest of these lakes is at Santee. Another is Indian Creek Reservoir, which receives the highly treated effluent from the South Tahoe plant. The third is at Lancaster in Los Angeles County.

Treatment beyond conventional organic removal is necessary for recreational reuse. It is essential that the oxygen demand be maintained low enough to sustain the necessary dissolved oxygen, that nutrients be kept below levels causing excessive algal blooms, that ammonia be almost totally absent, that pathogens be essentially absent, and that any toxic substances be kept at very low levels. At Santee, water (usually of satisfactory quality) is obtained by lagoon-treating activated sludge effluent, percolating through natural gravel beds, and chlorinating. The South Tahoe treatment system includes activated sludge followed by two-stage lime treatment, ammonia stripping, filtration, carbon treatment, and chlorination. The Lancaster system includes oxidation ponds, chemical treatment with alum, filtration, and chlorination. Some typical values of important effluent parameters are shown in Table 4.

TABLE 4. TYPICAL PERFORMANCE OF PLANTS PRODUCING RECREATIONAL WATER FROM WASTEWATER

Parameter	Santee	Tahoe	Lancaster
Turbidity, JTU	5	0.3 - 0.5	1.5
Ammonia nitrogen, mg/l	0.4	23 - 35	1.0
Nitrate nitrogen, mg/l	1.0	0.1 - 0.9	1.9
BOD, mg/l	3.5	0.7 - 3.2	0.4
Total phosphorus, mg/l	3.6	0.2 - 0.4	0.29
Coliforms, MPN/100 ml	< 2	< 2	< 2.2

The cost for treatment by these plants varies widely. The minimum cost of 15¢/1000 gal was reported at Lancaster in 1971. The reported cost at Santee was 45¢/1000 gal, and at Tahoe, it was 88¢/1000 gal.

In all cases, the water from the lakes is further used in varying degrees for irrigation.

DOMESTIC REUSE

The capability of reusing wastewater for all domestic purposes has a number of important advantages over lower quality reuses. The most significant advantage is the ability to transport the water to be reused in the same distribution system as the original water supply. The necessity of providing a separate distribution system has undoubtedly had a very restrictive effect on reuse.

In the United States no reuse system has yet been developed that has been approved for deliberate potable reuse. The ability to treat wastewater to a high degree of purity exists, but there are no clearcut standards of potability with which to compare the quality of the water. U.S. drinking water standards are not presently complete enough to be utilized with a renovated wastewater. The two types of contaminant groups that present the greatest problems in potable reuse are trace organics and pathogens, especially viruses. Fortunately, progress is being made in developing analytical techniques for both trace organics and viruses. As a result, answers are beginning to be obtained to the questions raised by public health authorities concerning potable reuse.

A number of water-short communities have expressed interest in potable reuse. Denver, Colorado, has taken the greatest initiative toward reuse, including construction of a 1-mgd pilot plant by 1980. Assuming favorable results, they plan to implement large-scale reuse by 1990.

The only recognized potable reuse plant in the whole world is that at Windhoek, South-West Africa. This plant has operated intermittently for more than 5 years. Although there have been plant operating problems, there is no evidence that the product water has been responsible for any health problems. Public health authorities in the United States have not placed much reliance on the results of the Windhoek experience. They generally express the opinion that much more information on water quality and system reliability is needed.

The true driving force that will eventually bring about reuse is economics. When the cost of renovating wastewater becomes measurably less than the cost of alternative sources, interest will increase rapidly. At present, even in many arid areas, reasonably priced alternative sources have not been exhausted. An ongoing study of a number of specific cases is providing interesting information concerning conditions conducive to reuse. It appears under present economic conditions that reuse will not usually be competitive with water imported in large aqueduct systems. The most favorable situation for reuse is in areas of low rainfall where the water supply is from wells. In the arid Southwest it is common for communities using wells to be withdrawing water faster than it is being recharged. It is in these communities that reuse is likely to be required. In addition, there are cases such as Denver, Colorado, and even some cities in the humid eastern part of the country that, because of local conditions, may have to consider reuse.

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